CHARACTERIZING ORGANIC MATTER AND NUTRIENT STATUS IN SMELTER-AFFECTED SOILS

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ABSTRACT

Forest vegetation dieback has occurred around Flin Flon, Manitoba and Creighton, Saskatchewan since the beginning of the 20th century, when sulphide ore smelting began in the area. In order to support future revegetation strategies, evaluation of soil organic matter (SOM) quality and quantity and soil nutrient status variation in the area is necessary. This study focused on the spatial variation of SOM and soil nutrient status, particularly in relation to percentage plant (ground and woody species) cover. Soil nutrient status and other soil properties were also evaluated based on direction around the smelter.

To identify spatial variation of SOM and soil nutrient properties, two 3-km transects were established North and South of the smelting stack and soil samples were collected every 100 m. To identify variation in soil nutrients and other properties based on direction around the smelter, eight 200-m by 200-m grids were established at each cardinal and ordinal direction, 3-km from the smelter. Soils were classified as mineral or organic, and percentage ground species and woody species cover was measured at each sample point. Transect samples were analyzed for SOM fractions including light fraction (LF) weight, LF and heavy faction (HF) carbon (C) and nitrogen (N) content, water extractable organic carbon (WEOC) and total dissolved nitrogen (TDN). Whole soil samples from the transects and grids were analyzed for total organic C (TOC), total N (TN) and total sulphur (TS), as well as exchangeable cations, cation exchange capacity, base saturation, pH and clay content. Transect data was analyzed with non-metric multidimensional scaling and ordination to determine significant variables related to percentage ground and woody cover and/or distance from the smelter, for mineral and organic soils separately. Differences in soil characteristics between grids were identified using Kruskal-Wallis analysis of distribution and the median test of independent samples.

Results varied depending on mineral or organic soil classification. Percentage ground and woody species cover ranged from 0% to 90%. Light fraction and HF results were within a range seen in previous boreal forest studies and had median C to N of ~ 30 – 45 and ~20 - 30 for LF and HF, respectively. Low values of WEOC (mineral soil median between ~ 2 to 5 mg C kg^{-1} soil; organic soil median between ~ 28 to 60 mg C

kg^{-1} soil) and TDN (mineral soil median between ~ 0.4 to 1 mg N kg^{-1} soil; organic soil median between ~ 4 to 9 mg N kg^{-1} soil) were identified. Non-metric multidimensional scaling and ordinations indicated the significant variables related to plant cover varied between mineral and organic soils. In mineral soils, cation and cation exchange variables were most significantly (P = 0.001) correlated to ordinations; however, percentage ground species and woody species cover vectors grouped with SOM quality and quantity vectors (LF-C:N, HF-C:N, LF-N and TDN) indicating SOM variables are more related to plant cover than other variables analyzed. In organic soils, trends were less obvious and may be masked by the intrinsic pedologic properties that define organic soils. Areas with low plant cover had lower SOM C:N and higher TN, likely attributed to more decomposed (recalcitrant) SOM. Total nutrient status of whole soils did not effectively explain inconsistent vegetation cover; and exchangeable cation content, cation exchange capacity and base saturation may reflect other disturbances. The soil issues hindering revegetation in the area are complex and multi-faceted; however when planning revegetation strategies in the area it is suggested using LF, WEOC and TDN SOM fractions to identify SOM quality and quantity variation.

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LIST OF ABBREVIATIONS

BS – Base saturation

CEC – Cation exchange capacity

CECe – Effective cation exchange capacity

C:N – Carbon to nitrogen ratio

DOM – Dissolved organic matter

FT-IR – Fourier transform infrared

HBMS – Hudson Bay Mining and Smelting Co., Limited

HF – Heavy fraction

HF-C – Heavy fraction carbon

HF-C:N – Heavy fraction carbon to nitrogen ration

HF-N – Heavy fraction nitrogen

LF – Light fraction

LF-C – Light fraction carbon

LF-C:N – Light fraction carbon to nitrogen ratio

LF-N – Light fraction nitrogen

LF-Wt – Light fraction weight

MB – Microbial biomass

MB-C – Microbial biomass carbon

MB-N – Microbial biomass nitrogen

NMDS – Non-metric multidimensional scaling

OM – Organic matter

SOM – Soil organic matter

SO_2 – Sulphur dioxide

TDN – Total dissolved nitrogen

TN – Total nitrogen

TOC – Total organic carbon

TS – Total sulphur

WEOC – Water extractable organic carbon

WEOM – Water extractable organic matter

1. INTRODUCTION

Loss of vegetation and soil quality is common in the boreal forest, where industries based on the mining and harvesting of petroleum, lumber and metal-containing ore (and other commodities) are present. In Canada, one such area is the boreal forest surrounding Creighton, Saskatchewan and Flin Flon, Manitoba, where mining for non-ferrous metals has occurred since the early 20th century. In addition to mining, smelting operations owned and operated by Hudson Bay Mining and Smelting Co., Limited (HBMS) were operational in the Flin Flon-Creighton area from 1930 until June 2010. The smelting complex extracted copper (Cu), zinc (Zn) and cadmium (Cd) through heating and chemical treatment of sulphide ore. Byproduct emissions of the smelting process in the area included sulphur dioxide (SO_2) and several trace metals, including Zn, Cu, lead (Pb), arsenic (As), Cd and mercury (Hg). Several studies have identified trace metal deposition as far as 100 km from the smelting stack (Zoltai, 1988; Henderson et al., 1998; McMartin et al., 1999) and Franzin et al. (1979) estimated that approximately 250,000 km^2 of area around the smelter have been affected by particulate metal deposition from the smelter.

The specific effects of smelter and mining related operations on the surrounding forest environment cannot be directly identified; however, forest dieback has occurred within an approximately 3 km radius around the smelter and there are physical, chemical and biological symptoms of soil depletion. The changes to the forest environment around Flin Flon-Creighton are similar to those identified surrounding many other non-ferrous smelting facilities (Ginocchio, 2000; McMartin et al., 2002; Viventsova et al., 2005; Anderson et al., 2009). A review by Kozlov and Zvereva (2007) referred to the areas around non-ferrous smelters as "industrial barrens," where vegetation loss and alteration of soil properties has negatively impacted the productivity of the surrounding forest environment. Additionally, the review identified several patterns of environmental degradation occurring at non-ferrous smelting sites, including: bare landscapes with metal contaminated soil; sparse vegetation; soil erosion; and exposed bedrock; changes to micro-climate; and hindrance of nutrient cycling.

In response to the altered forest environment that has developed in Flin Flon-Creighton, a local initiative called *The Green Project* has been treating bare soil surfaces with dolomite limestone since 1999. The goal of the project is to increase soil pH and prompt regeneration of forest vegetation. Such revegetation strategies have been successful in other areas, such as Sudbury, Ontario (Winterhalder, 1995b; Winterhalder, 1995a); however, in Flin Flon-Creighton revegetation has not been successful at all treated sites. In order to facilitate more widespread forest revegetation across the Flin Flon-Creighton area, *The Green Project*, in collaboration with HBMS, approached the University of Saskatchewan Department of Soil Science to develop a multi-faceted project focused on understanding the local soil environment. The overall project within the Department of Soil Science, which commenced in 2008 with a soil survey of the area, aims to identify key soil properties and subsequently develop additional soil treatment strategies that will increase revegetation success.

Some soil properties, that may be contributing to the inconsistent natural and assisted plant regeneration in the area, include soil organic matter (SOM) quality and quantity, as well as overall soil nutrient status. For the purpose of this study, SOM quality is identified by the amount of labile (readily decomposed) SOM fractions, as well as the carbon (C) to nitrogen (N) ratio (C:N) of those fractions. Soil organic matter quantity is identified by the amount of C and N within analyzed fractions, as well as by weight (where applicable). Nutrient status of whole soils is defined by total organic C (TOC) and total N (TN) content, soil C:N and total sulphur (TS) content. These indices are similar to those used in studies conducted in smelter-impacted areas, which found that soil TN, SOM and soil pH best explained variation of plant growth (Ginocchio, 2000) and attributed reduced nutrient cycling to altered soil microbial populations as the cause for poor vegetation growth immediately surrounding a smelter (Kiikkila, 2003). Furthermore, in Flin Flon-Creighton specifically, Winterhalder (2003) identified the accumulation of less decomposed, recalcitrant (not readily decomposed) SOM as possible contributors to inconsistent vegetation response to liming.

Therefore, in order to determine how SOM quality and quantity varies throughout the Flin Flon-Creighton area, this study will focus on spatial variation in SOM,

particularly in relation to percentage vegetation (ground and woody species) cover. The specific objectives and hypotheses of this study are:

Objective 1a: Evaluate variation in SOM quality and quantity and soil nutrient status in relation to distance along transects established north and south of the HBMS smelter.

Hypothesis: Soil quality, TOC and TN of whole soil samples and SOM fractions will be positively correlated with distance, whereas total sulphur (TS) content of whole soil samples will be negatively correlated with distance.

Objective 1b: Evaluate the variation in SOM quality and quantity and soil nutrients in relation to percentage ground and woody cover along transects established north and south of the HBMS smelter.

Hypothesis: The quality, TOC and TN of whole soil samples and SOM fractions will be positively correlated with plant cover.

Objective 2: Identify the variation of plant cover, soil nutrients and general soil properties at each cardinal and ordinal direction, by analysis of grid soil samples.

Hypothesis: Plant cover and analyzed soil parameters are unaffected by ordinal or cardinal direction from the HBMS smelter.

Findings from this study will identify variations in the nutrient status of SOM and whole soil samples, as well as in other properties that reflect the capacity for soil to sustain vegetation, in relation to distance from the smelter, ground species cover, woody species cover and direction. The overall findings also will support the development of future eco-restoration and revegetation strategies in the Flin Flon, MB and Creighton, SK area.

2. LITERATURE REVIEW

2.1 Non-Ferrous Base Metal Smelting Deposition

Most non-ferrous smelters are found in the northern hemisphere (North America and Russia) where ore resources are abundant in non-iron metals, including copper (Cu,) nickel (Ni), zinc (Zn) and lead (Pb) (Kozlov and Zvereva, 2007). Many of these facilities began operating in sulphide-ore based forested areas (boreal, mixed or hardwood) within the last 150 years and, through aerial deposition of sulphur dioxide (SO_2) and trace metals, have contributed to the depletion of chemical and physical soil characteristics and the ability of the soil to sustain plant growth. This is manifested in barren landscapes with minimal vegetation, amplified erosion and trace metal accumulation in soils (Derome and Nieminen, 1998; Ginocchio, 2000; Kiikkila, 2003; Viventsova et al., 2005; Anderson et al., 2009). Metal and SO_2 inputs from smelting, however, often occurred after other disturbances (such as deforestation and forest fires) thereby exacerbating the destruction of an already sensitive environmental system (Kozlov and Zvereva, 2007).

In Canada, metal deposition from emissions has been one of the most widely studied environmental issues in relation to smelting operations. Studies have found an increase in smelter-related metals in soil samples taken within close proximity to a smelter (Henderson et al., 1998; McMartin et al., 1999; McMartin et al., 2002; MacDonald and Hendershot, 2003), and also in peatland samples (Gignac and Beckett, 1986; Zoltai, 1988), vegetation tissue (Wotton et al., 1986) and precipitation (Franzin et al., 1979). However, the conditions required for considerable metal accumulation are not straightforward. A study of metal deposition in Sudbury, Ontario (Ni smelter) and Rouyn-Noranda, Quebec (Cu smelter) identified that accumulation of smelter-derived metals in forest soils was not directly related to proximity to the smelter, but rather that soil characteristics (organic matter content, parent material, soil formation processes) and variability of metal deposition influence the amount and type of metal accumulation (MacDonald and Hendershot, 2003). Furthermore, McMartin et al. (2002) identified several patterns in metal accumulation in forest soils surrounding Rouyn-Noranda, Quebec (Cu smelter), Flin Flon, Manitoba (Cu-Zn smelter), Trail, British Columbia (Pb-Zn smelter), and Pinchi Lake, British Columbia (Hg mine). At all sites, metal

accumulation in humus (organic surface layers) decreased with distance from smelters. In Flin Flon and Rouyn-Noranda, mineral B horizons at points within 10 km of the smelters also had metal accumulation. At other the smelter locations, however, metal accumulation in the B horizon was a factor of organic matter content and geology, and at all locations, the metal content in the mineral C horizon was analogous with bedrock geochemistry. In addition to research on smelter-derived metal accumulation in forest soils, studies have identified the impact of metal accumulation and other smelter-related issues on various forest soil and vegetation properties.

2.2 Degradation of the Boreal Forest Soil Environment Due to Non-Ferrous Smelting Inputs and Associated Disturbances

2.2.1 Vegetation

Suppressed vegetation growth has been identified in many of the areas where smelter-derived metal accumulation has occurred. In Harjavalta, Finland, an area between 0.5 km to 1 km surrounding the smelter had very little vegetation, as well as reduced flora and fauna biodiversity within 4 km (Kiikkila, 2003). In Anaconda, Montana, vegetation cover at smelter-affected sites ranged from 51% to 99% and was comprised of mostly grasses with few forbs or trees (Anderson et al., 2009). Reduced vegetation growth in close proximity to a smelter in the Kola Peninsula in Russia led to reduced biomass inputs into soil and an increase in evaporation and erosion (Viventsova et al., 2005). High metal accumulation in peatland soils within close proximity to a Sudbury, Ontario smelter was coupled with decreased/damaged vegetation (Gignac and Beckett, 1986). Specifically, a 10 km area surrounding the smelter had vegetation damage, with the number of species increasing with distance from the smelter, and *Sphagnum* species increasing between 12 km and 30 km. The same study also found that where there was an absence of *Sphagnum* species, the hydrology changed and resulted in a lower water table and colonization by drought-tolerant vegetation. Wotton et al. (1986) found Ni accumulation in conifer cones in areas near the Thompson, Manitoba smelter, and seedling growth was inhibited (possibly due to metal toxicity) within a 5 km area around the smelter.

2.2.2 Soil organic matter

Soil organic matter is composed of non-living plant, animal and microbial material varying in degree of decomposition and mobility. The primary function of SOM is to serve as an energy substrate for plant and soil microbial communities; however it also enhances soil aggregation and water retention, cation exchange capacity and pH buffering (Christensen, 1992; Baldock and Nelson, 2000). Through decomposition and mineralization, microorganisms convert SOM into inorganic nutrients [e.g., C, N, phosphorus (P), S] that are further utilized by soil microorganisms and vegetation. As decomposition progresses, microorganisms exploit the most labile (readily utilized) SOM fractions, which are broken down into smaller, more recalcitrant (less readily decomposed) structures. The availability of SOM fractions to microorganisms is, however, dependent on various physical and chemical aspects of the soil strata, as well as the decomposition state of the SOM. Decomposition of labile fractions (which reflect the C:N and chemical structure of the originating material) are most strongly influenced by soil aggregation and pore size, and are more protected in a strongly aggregated soil matrix. The decomposition of recalcitrant fractions (e.g., lignin and alkyl compounds) are influenced by soil chemistry and are more protected in soils with high base cation and aluminum and iron oxide content (Baldock and Skjemstad, 2000). Furthermore, Oades (1988) discussed several soil factors influencing C mineralization and SOM turnover, and concluded that conditions favouring rapid turnover include high temperature, high inputs of nutrient and carbohydrate rich biomass, coarse (sandy) soil texture, low pH and low soil surface charge. Therefore, the combination of environmental conditions with physical and chemical soil characteristics affect the amount and lability of SOM fractions present in the soil environment and subsequent availability to microorganisms and plants.

Many aspects of the soil environment and subsequent ecosystem functioning (e.g., microorganism and vegetation productivity) are influenced by and interact with SOM, therefore it is important to identify the quantity and quality of SOM present. This identification is especially important in anthropogenically-disturbed environments (such as smelter-affected forest areas) suffering from soil degradation. Although SOM quantity is dictated by plant, animal and microbial inputs, as well as microbial turnover and immobilization, SOM quality can be defined in several ways. For example, Gregorich et

al. (1994) identified the amount of TOC and TN, light fraction (LF) SOM, mineralizable C and N, microbial biomass, carbohydrates and enzymes as quality indicators, but that the choice of indicator should be made to address the process (soil structure, nutrient storage, turnover) being investigated. In addition, the TN (and associated C:N) and recalcitrance (lignin content) of the organic substrate has been used in reference to potential mineralization and, therefore, quality in forest soils (Attiwill and Adams, 1993). However it was further discussed that the measurement of TN itself does not identify whether the N is in a labile or recalcitrant fraction. In addition, as previously discussed, physical availability of SOM to microorganisms identifies susceptibility to decomposition; therefore the amount of labile SOM fractions that are mobile or not strongly associated with soil minerals also reflects upon quality.

Based on this, and in order to characterize SOM based on quantity and quality, various physical and chemical fractionation methods (as well as microbial biomass measurements) are useful (McLauchlan and Hobbie, 2004; von Lutzow et al., 2007). A symposium on SOM fractionation indicated physical fractionation is well-suited for understanding SOM C and N cycling and chemical fractionation is well-suited for understanding interactions between SOM, nutrients and organic compounds within soil (Olk and Gregorich, 2006). These methods are operationally defined and therefore the pools isolated are a function of the methods used (Sollins et al., 1999).

Density Fractionation

Physical fractionation is based on the premise that SOM pools have dynamic and responsive relationships with soil mineral particles and the degree of association or adsorption with soil mineral particles often influences the lability of SOM (Christensen, 1992; Gregorich et al., 2006). Density fractionation is one method of physical fractionation of SOM and separates OM into at least two components using liquid of a specific density. The fractions isolated reflect varying degrees of SOM decomposition and recalcitrance (Christensen, 1992). Typically two SOM fractions are discussed: 1) light fraction (LF), which is lighter than the dense liquid; and 2) heavy fraction (HF), which is heavier than the dense fluid. The fluid density used for the analysis varies and is selected based on soil type. The appropriate density can be identified when the C:N of the LF, HF and whole soil are all different, thus ensuring fractions isolated are unique SOM

pools (Pare and Bedard-Haughn, 2011). Light fraction SOM is thought to reflect more recently decomposed and potentially labile material; whereas the HF is more mineral-associated and potentially recalcitrant material (Christensen, 1992; Christensen, 2001; Gregorich et al., 2006).

In a Boreal Forest Transect Case Study project, which spanned the boreal forest of Saskatchewan and Manitoba, the LF C:N (~ 40 to 60) was higher than the C:N of soil LFH horizons or mineral fractions (< 20 to 40), and increased with depth in the soil profile (Norris et al., 2011). Overall findings of the study identified a climatic gradient with respect to organic C in forest soils and that the northern-most boreal forest soils had higher amounts of labile organic C in whole soil. In a study of mineral soil in an old growth coniferous site in Oregon, the percent of total OM (by mass) recovered of LF and HF was 3.6% and 96.4%, respectively and the LF had a C:N of 60.7 (i.e., 28.7 % C and 0.5% N) (Crow et al., 2007). The HF had a C:N of 29.9 (i.e., 4.9% C and 0.2% N) and the C:N, %C and %N of the HF SOM was similar to that of the whole soil samples.

A review of density fractionation literature discussed that LF C and N quantities are affected by changes in land use, vegetation type, climate and other factors that influence decomposition and litter input (Christensen, 2001). In forest environments, the LF has been found to respond to disturbance; and of the physical fractions isolated, the LF has been strongly correlated with total carbon (TC) and TN cycling in the soil (He et al., 2008). A laboratory study conducted on soils from agriculture and forest ecosystems found C and N mineralization in forest soils was higher in minimally disturbed versus disturbed soils for both whole soil and LF samples, and the LF C:N ratio was higher (and more recalcitrant) in disturbed soils (Whalen et al., 2000). In addition, they found more N was mineralized in the HF of disturbed soils and overall findings indicated HF as a source of N and LF as a sink.

Although little research has been done to identify the effects of smelter emissions on LF and HF SOM, some smelter studies identified general trends in OM components of soil samples. Around a smelter in northeast Brazil, Klumpp et al. (2003) identified highest organic carbon (OC) content at sites closest to the smelter, which was attributed to OM accumulation caused by suppressed microbial decomposition from S and other pollutants in the soil. Viventsova et al. (2005) analyzed SOM functional groups (e.g.,

carboxylic and phenolic molecules) using fourier transform infrared (FT-IR) spectroscopy and found the number of SOM functional groups decreased with closer proximity to the smelter. This was attributed to long-term metal contamination, which caused a reduction in biomass inputs and increased SOM-metal binding leaving SOM unavailable to microorganisms or vegetation. In contrast to these findings, Anderson et al. (2009) found that SOM content measured by loss on ignition was unrelated to metal content in soil.

Water Extractable Organic Matter

Chemical fractionation methods also can be used to isolate SOM that is labile, mobile in soil solution and readily available to plants and microorganisms. One such SOM fraction is water extractable organic matter (WEOM), which is isolated by extraction with aqueous (water or weak salt) solutions (Herbert and Bertsch, 1995; Zsolnay, 1996; Chantigny, 2003). The term WEOM is often used synonymously with dissolved organic matter (DOM); however, DOM is a general term that encompasses SOM present in micro, meso and macro soil pores (although extraction using lysimeters or by leaching from columns in the laboratory generally isolates mobile DOM present in macropores) (Zsolnay, 1996; Zsolnay, 2003). In contrast, WEOM is generally representative of SOM in macro and, to a lesser extent, mesopores and is only a fraction of the broad-term DOM. In addition, due to the nature of extraction and influences of distilled water on soil aggregates and microbial cells, WEOM values are generally larger than those of DOM isolated by lysimeters or leaching (Chantigny, 2003). As a consequence, it is incorrect to directly compare WEOM and DOM data although both fractions represent SOM that has rapid turnover and is readily available to soil microorganisms and vegetation.

In a review of WEOM research in various soil environments, water extractable organic carbon (WEOC) content in mineral forest soils ranged from 10 to 650 μg C g^{-1} soil dry weight to and in organic soils ranged from approximately 1000 to 2400 μg C g^{-1} soil dry weight, depending on sample preparation and extraction solution (Zsolnay, 1996 and sources within). In addition, Norris et al. (2011) identified that WEOC was the greatest contributor to SOM in the C horizon of a boreal forest soil at higher latitudes, identifying the importance of WEOC to SOM deep in the soil profile. It is due to this

highly mobile and labile nature that WEOM is a good index for SOM quality and quantity from a plant nutrition perspective. As discussed in Chantigny (2003), WEOM content in soil is greatly influenced by land use and management practices (e.g., clear-cutting, cultivation, liming and fertilizer application) regardless of the environment type (forest, grassland, arable soil). Vegetation type also reflects WEOM composition (and vice versa) (Smolander et al., 2005).

In addition, due to the chemistry and sorptive ability of organic compounds in soil solution, contaminants and metals may be transported through the soil strata while bound to WEOM; however the extent of this is dependent on WEOM mobility and sorption to mineral particles (Herbert and Bertsch, 1995). In a study looking at smelter-affected soils in Quebec, WEOC was identified as the main characteristic controlling the amount of water-extractable metals present in soils (Seguin et al., 2004). Furthermore, the amount of WEOC present in samples increased with distance from the smelter, which the authors attributed to the affect of pH (which also increased with distance) on OM decomposition. Therefore, as soil environmental conditions impact the composition and mobility of WEOM, influences the mobility of contaminants and metals in soil solution.

Soil Microbial Biomass

Understanding rates of SOM turnover requires identification of the size and activity of microbial populations. As previously mentioned, the soil microbial population is a necessary soil component in regards to SOM turnover and decomposition and subsequent nutrient cycling for plant uptake. Large quantities of soil nutrients (C, N, P and S) are present in soil as microbial biomass (MB) and through MB measurement via chloroform fumigation-extraction (Voroney et al., 2008) contributions to SOM can be quantified. As reviewed by von Lutzow et al. (2007), studies have indicated MB fractions within soil vary depending on ecosystem, land use, soil texture and degree of biomass pool protection. In addition, studies conducted to understand the effects of heavy metal pollution on MB indicated a lower level of microbial activity and microbial biomass C and N (Dilly, 2006) and P (Khan et al., 2007) in heavily polluted soils. Another study measuring spatial variability of MB in relation to a smelter in Montana identified decreased MB at all affected sites, with the most adverse affects on MB occurring at sites in closest proximity to the smelter (Anderson et al., 2009).

2.2.3 Soil nutrient status

In comparison to deciduous forests, coniferous forest ecosystems, such as the boreal forest, have lower N mineralization (based on equivalent soil C content) and higher soil C:N (average 27.9 in coniferous versus 17.8 in deciduous) (Booth et al., 2005). Nitrogen is often the limiting factor in nutrient cycling in boreal forest systems where organic N is a major contributor to the overall N pool (Schimel and Bennett, 2004; Nasholm et al., 2009) and N limitation may be further exacerbated by changes to the boreal forest environment (Rennenberg et al., 2009). In Alaskan coniferous sites the soil C:N of surface A horizons was approximately 22 and increased with depth (Ping et al., 2010). In a review paper of studies on N characteristics of different ecosystems, Booth et al. (2005) found mineral soil C:N ratios for temperate woodlands ranged from < 10 to nearly 50; however the majority of results were between 10 and 30. In the same review, the majority of C content in mineral temperate woodland soils was between 2 and 20 g C kg^{-1} soil (0.2 to 2%) and the majority of soil N was between 1 and 10 g N kg^{-1} soil (0.1 and 1%).

Like cation exchange, however, nutrients (and the extent of nutrient cycling) in soils also vary depending on external influences. Research on nutrient dynamics in smelter-affected forest soils identified some patterns in relation to soil type and proximity to smelting stacks. In the Kola Peninsula, Russia, the low total soil C content in areas closest to a smelter was attributed to reduced biomass inputs due to lack of vegetation (Lukina and Nikonov, 2001). In contrast, Derome and Lindroos (1998) reported that total N content of organic surface soil layers did not differ based on distance, but soil sulphur increased with closer proximity to a smelting stack. Studies conducted in forest and grassland ecosystems in South America also identified higher total S in soils closer to a smelter (Ginocchio, 2000; Klumpp et al., 2003). Furthermore, Ginocchio (2000) found that total N increased with distance from a smelter and that the combination of total N, OM content and soil pH better explained the change in plant species abundance than soil S and Cu content.

2.2.4 Cation exchange

Soil cation exchange capacity (CEC) gives an indication of soil nutrients available for vegetation establishment and growth. The CEC, exchangeable cation content and

percent base saturation (%BS) of forest soils vary depending on many properties, including pH (Ross et al., 2008) and organic matter content (Ping et al., 2010). Several studies have measured CEC, exchangeable cations and %BS in smelter-affected soils, with varying results. In the Kola Peninsula in Russia, organic horizons in areas with the most extreme vegetation loss had the lowest values of CEC, calcium (Ca^{2+}), magnesium (Mg^{2+}) and potassium (K^{+}) which was attributed to low SOM content from reduced plant biomass inputs (Lukina and Nikonov, 2001). In soil surrounding a Cu^{2+} and Ni2 smelter in Harjavalta, Finland there was high Cu and Ni content in upper organic soil layers and the displacement of Ca^{2+}, Mg^{2+}, K^{+} and aluminum (Al^{3+}) to sub-surface mineral soil horizons (Derome and Nieminen, 1998). The same study found %BS decreased with proximity to the smelter, was very low in mineral samples and that Mg^{2+} in organic surface layers increased with closer proximity to the smelter (CEC, Ca^{2+}, K^{+}, Na^{+} and Al^{3+} were not related to distance). In contrast, Anderson et al. (2009) found higher CEC values in contaminated sites and values ranged between 14 and 33 $cmol_{(c)}$ kg^{-1} soil and varied based on soil texture. They also identified that Ca^{2+}content varied considerably among sites. These contrasting results between studies emphasize that conditions specific to certain environments (i.e., soil type, disturbance extent, natural disturbances, etc.) likely dictate the trends seen in cation and cation exchange capacity.

Other forest disturbances such as fire, clear cutting and point source pollution can also can affect the cation exchange capability of forest soils. Maximum values of effective cation exchange capacity (CECe) (72.5 $cmol_{(c)}$ kg^{-1} soil) and Ca^{2+} (57.6 $cmol_{(c)}$ kg^{-1} soil) and Mg^{2+} (11.9 $cmol_{(c)}$ kg^{-1} soil) have been identified within approximately 50 years of forest fire in a 250-year fire gradient in the boreal forest of northwestern Quebec (Brais et al., 1995). In addition, a review by Certini (2005) discussed a trend of high values of exchangeable Ca^{2+}, Mg^{2+} and K^{+} in soil after fire (albeit for a relatively brief time) and that soil CEC after forest fire is dependent upon the amount of organic matter remaining. The same review also identified %BS increases due to the release of base cations in freshly burned OM. In contrast to this, disturbances from clear cutting for lumber has lead to a reduction in soil CEC and cation content. In a study in a northern Saskatchewan mixed-wood forest, Pennock and van Kessel (1997) identified an eventual decrease in CEC and %BS following clear cutting. Specifically, CEC increased five years

after clear cutting, but after six to 20 years soil CEC was lower than values found in mature forest stands. Based on this, the CEC and cation content of smelter-affected soils may see adverse affects (i.e., CEC and cation content reduction) both from aerial deposition of particulates as well as from disturbances by related deforestation; however, forest fires natural to the area may ameliorate (i.e., increase CEC and cation content) some of these adverse affects.

2.3 Flin Flon, Manitoba and Creighton, Saskatchewan

The Flin Flon, Manitoba and Creighton, Saskatchewan areas were first explored for ore deposits in the early 19th century and, after discovering Cu ore in 1915, mining of mineral deposits began (Stauffer, 1974). The area is underlain by a zone of metavolcanic rock from the Flin Flon greenstone belt (Stern et al., 1995) and the sulphide ore present contains significant amounts of various metals. It was due to the presence of these metals that, in 1930, HBMS constructed a Cu, Zn and Cd smelter in the area, in addition to the mines already present. Initially, several 30 m tall stacks were utilized for exhaust release; however, after several upgrades, a single 251 m tall "superstack" was constructed and put into operation in 1974 (Franzin et al., 1979). The superstack was utilized until the smelter was decommissioned in June 2010.

During the time smelting occurred in the Flin Flon-Creighton area, several studies identified deposition and/or accumulation of various metals (including Zn, Cd, Pb, Hg, As and Cu, among others) and sulphate in soil and/or humus (organic soils) (Zoltai, 1988; Henderson and McMartin, 1995; Henderson et al., 1998; McMartin et al., 1999; McMartin et al., 2002; MacDonald and Hendershot, 2003), vegetation (Shaw, 1981) and precipitation (Franzin et al., 1979). All studies identified decreasing metal concentrations with increasing distance from the stack and identified smelter derived metals in organic surface horizons up to approximately 100 km away from the smelting facility. However, McMartin et al. (1997) and Hendershot et al. (1998) established that, at depth in mineral horizons, the presence of metals at concentrations exceeding natural geochemical levels only existed at sites within a 10 km radius of the smelter, and attributed this to leaching from organic-enriched surface horizons. Zoltai (1988) identified the highest concentrations of Zn, Pb, Cu, As, iron (Fe), aluminum (Al) and sulphur (S) in the surface

of peat soil occurred within 5 km of the smelter stack and that the presence of metals at depth was actually the result of peat accumulation since the commencement of smelting operations.

Although the deposition and accumulation of smelter-derived metals and sulphate has been well documented in the area, improvement of smelting techniques led to declining emissions up until the closure of the smelter in 2010. According to the HudBay Minerals Corporate Social Responsibility Report for 2009 (HudBay Minerals Inc, 2009), SO_2 and particulate emissions were the lowest in at least four years – 1,435,000 tonnes of SO_2 and 900,000 tonnes of particulate emissions. Regardless of continued smelting improvements, however, the immediate area surrounding Flin Flon – Creighton has experienced long-term forest vegetation loss and reduced vegetation regeneration similar to what has been identified in several other smelter-affected areas (Winterhalder, 1995a; Ginocchio, 2000; Kiikkila, 2003; Viventsova et al., 2005).

It was in response to this forest vegetation loss that, in 1999, a volunteer based community organization – *The Green Project* – was established to attempt amelioration of soil acidity conditions through dolomite limestone application. As of 2009, *The Green Project* had spread dolomite limestone on 42.5 ha of land throughout the Flin Flon-Creighton area. The late Dr. Keith Winterhalder, who had been involved in similar revegetation efforts in smelter-affected areas surrounding Sudbury, Ontario (Lautenbach et al., 1995), initially spearheaded the project. Dr. Winterhalder published some work on revegetation efforts in Flin Flon-Creighton and concluded that although limestone application was successful in numerous areas, other sites were not responsive to treatment regardless of normal forest soil pH levels (Winterhalder, 2003). Winterhalder hypothesized this inconsistent responsiveness to liming may have been caused by variations of metal availability and the accumulation of undecomposed organic matter. In addition, revegetation as monitored by *The Green Project* members identified inconsistent variability in extent of success; namely several sites north, as well as sporadic sites south and west of the smelter had the lowest revegetation success (Price, 2009). It was in response to this inconsistent success at revegetation attempts that the Department of Soil Science at the University of Saskatchewan became involved in the overall revegetation strategy in the area. Through collaboration with *The Green Project*

and HBMS, the overall project conducted by the University of Saskatchewan Department of Soil Science aims to understand the soil environment in the Flin Flon-Creighton area and identify soil treatments that will improve the re-greening process. The project discussed in this manuscript specifically focuses on determining spatial variation in SOM quality and quantity with respect to percentage ground and woody species cover.

3. MATERIALS AND METHODS

3.1 Study Site

The study took place during the summer of 2009, in areas surrounding Flin Flon, Manitoba and Creighton, Saskatchewan, Canada (55°N, 102°W), located on the Manitoba-Saskatchewan border approximately 600 km northeast of Saskatoon, SK and 800 km northwest of Winnipeg, MB. Flin Flon-Creighton is located in the boreal shield ecozone of Canada, stretching from northern Saskatchewan to Newfoundland (Natural Resources Canada, 2007). The natural landscape of the boreal shield is characterized by exposed rock outcrops, nutrient-poor, acidic soils, and wetland areas typical of poor drainage conditions. Typical soils in well-drained areas include Brunisol and Grey Luvisols and those in poorly drained areas include Gleysol and soils of the Organic order (Eilers and Swidinsky, 1989). The climate is characterized by long, cold winters and short, cool summers and, indicative of this climate, the mean annual temperature for Flin Flon between 1971 and 2000 was 0.6°C (Environment Canada, 2010). Typical trees present in the western boreal shield include black spruce (*Picea mariana*), white spruce (*Picea glauca*), jack pine (*Pinus banksiana*), tamarack (*Larix laricina*) and balsam fir (*Abies balsamea*). Understory may include a variety of shrubs, wildflowers, moss and lichens (Johnson et al., 1995).

As summarized by Stauffer (1974) and Stern et al. (1995), the complex geology of the Flin Flon-Creighton area, referred to as the Flin Flon greenstone belt, is comprised of metavolcanic, sedimentary and medium-grade metamorphic rocks. The greenstone belt, which contains massive sulfide ore deposits rich in copper, zinc and gold, attracted the attention of Hudson Bay Mining and Smelting Co., Ltd. who began mining and smelting operations in 1930 (Stauffer, 1974). Smelting facilities initially utilized short stacks, which were approximately 30 m in height; however in 1974 HBMS replaced the short stacks with one “super stack” approximately 251 m in height (Franzin et al., 1979). The super stack was decommissioned in June 2010 and all smelting operations in Flin Flon have since ceased.

3.2 Sample Design

As displayed in Fig. 3.1, transect and grid schemes were utilized for soil sampling, based on the objectives discussed in Section 1. The soils were analyzed to determine physical, chemical and biological characteristics; however, for any given sample the specific analyses varied depending on the origin and depth of sample. Table 3.1 lists the analyses conducted, as well as the samples to which the analyses pertain.

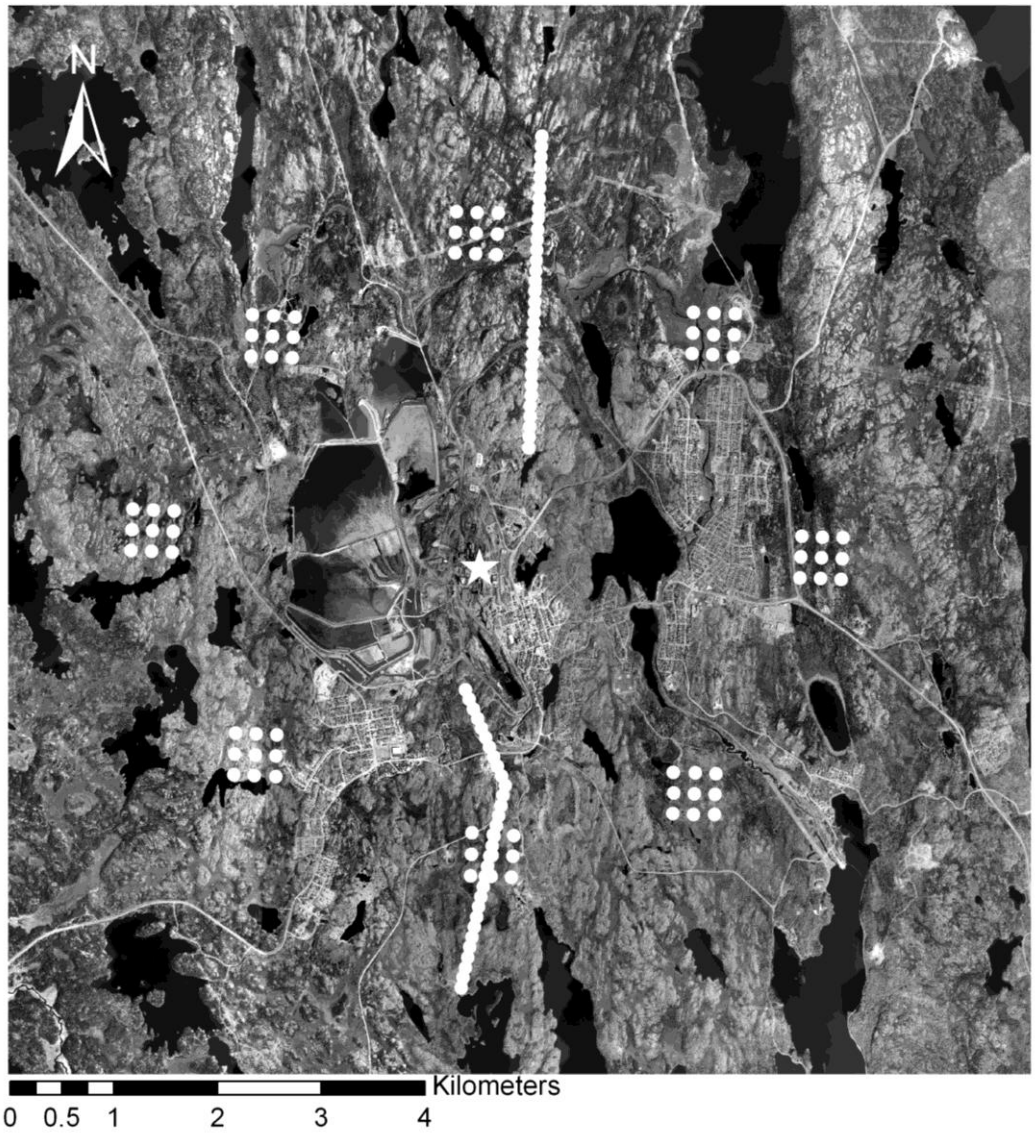

Fig. 3.1. North and south transects (n = 31 per transect) and cardinal and ordinal grid (n = 9 per grid) sampling points in the Flin Flon-Creighton area. Dots indicate a sample point and the star identifies the smelting stack.

Table 3.1. Laboratory analyses carried out on transect and grid surface (0- to 5-cm) and sub-surface (5- to 15-cm) samples.

Soil Analysis†	Grid Samples	Transect Samples	
	0- to 5-cm	0- to 5-cm	5- to 15-cm
SOM FRACTIONATION			
Chloroform Fumigation-Extraction			
-microbial biomass carbon	-	✓	-
-microbial biomass nitrogen	-	✓	-
Density Fractionation			
- light fraction carbon and nitrogen	-	✓	-
-heavy fraction carbon and nitrogen	-	✓	-
Water Extractable Organic Matter			
-water extractable organic carbon	-	✓	✓
-total dissolved nitrogen	-	✓	✓
SOIL NUTRIENT ANALYSIS			
-total organic carbon	✓	✓	✓
-total carbon	✓	✓	✓
-total nitrogen	✓	✓	✓
-total sulphur	✓	✓	✓
SOIL CHARACTERISTICS			
-pH	✓	✓	✓
-total cation exchange capacity	✓	✓	✓
-extractable Cations	✓	✓	✓
-effective cation exchange capacity	✓	✓	✓
-% base saturation	✓	✓	✓
-particle size (mineral samples only)	✓	✓	✓

†A "✓" indicates an analysis was carried out for the identified sample, a "-" indicates the analysis was not carried out.

Objective 1: Transect Design. To identify relationships between soil variables and distance from the stack, two 3-km long transects, running north and south, were established starting at 1-km north and 1-km south of the HBMS smelter stack. Soil samples were collected below the LFH layer (where present), at 0- to 5-cm ("surface") and 5- to 15-cm ("sub-surface") depth increments, at 100 m intervals (n = 124; 31 locations × 2 depths × 2 transects). Note: east/west transects were not possible due to restrictions imposed by industrial and municipal property, and 3-km transect distances were selected to encompass areas of both dieback and regeneration.

Objective 2: Grid Design. To address possible variations in soil variables based on direction relative to the stack, eight 200-m × 200-m grids were established at distance of 3 km from the stack in each cardinal and ordinal direction. Soil samples (0- to 5-cm; n = 72) were collected at nine points per grid.

3.3 Site Characterization

At each sample location, percentage ground species cover and percentage woody species cover were measured within a 3-m radius of the sampling point using visual cover estimation; plant species, soil parent material and other landscape characteristics also were identified. Each pit was classified based on the Canadian System of Soil Classification (Soil Classification Working Group, 1998) and depth to groundwater and bedrock was identified, where possible.

3.4 General Soil Characteristics

All samples were measured for pH, particle size distribution (mineral soils), effective cation exchange capacity (CECe), CEC and %BS. Soil gravimetric moisture content was measured as percentage water loss from 5 g of field moist soil after oven drying at 105°C for 24 h. For other soil analyses [excluding MB, WEOC and total dissolved nitrogen (TDN)], samples were air-dried at room temperature for approximately one week. Organic samples were ground to 2 mm and mineral samples were ground and then sieved to 2 mm after coarse fragment estimation. Coarse fragment content of mineral soil samples was measured as the volume of rocks larger than 2 mm, as a percentage of total soil volume, based on visual estimation after sieving.

Soil pH was measured with a sympHony meter and sympHony™ Gel 3-in-1 pH electrode (VWR International, USA) using double deionized water at a 1:2 (w/w) soil to water ratio for mineral soils and 1:10 (w/w) for organic soils (Hendershot and Lalande, 2008). Particle size distribution of mineral soil samples [< 17% TOC (Soil Classification Working Group, 1998)] was measured via laser diffraction using a LA-950 Laser Scattering Particle Size Distribution Analyzer (Horiba Instruments Inc., California USA). To remove organic matter prior to analysis, approximately 5 g of each soil sample was pretreated three to five times with 10 mL sodium hypochlorite (NaClO; pH = 8.5) (Anderson, 1963; Omueti, 1980; Mikutta et al., 2005) until organic matter was removed, as indicated by lack of effervescence. Replicate soil samples (n = 2) were analyzed every twenty samples and three soils of known texture (clay loam, silt loam and sandy loam) were analyzed for quality assurance and quality control.

Due to the acidic pH of the soil samples and the need to measure both mineral and organic samples using the same techniques, soil exchangeable cation content and total CEC were determined according to Meyer and Arp (1994), modified based on Schoning and Brummer (2008) and Skinner et al. (2001). Soil samples were extracted using 1 *M* ammonium chloride solution (NH_4Cl) at a 1:40 soil (g air-dried) to solution (mL) ratio. The soil-NH_4Cl suspension was agitated at 150 rpm for 24 h, filtered through Whatman 42 filter paper and analyzed for extractable calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}) and aluminum (Al^{3+}) by flame atomic absorption spectroscopy (Spectra AA220 Atomic Absorption Spectrometer; Varian Australia Pty Ltd., Mulgrave, Victoria Australia). Soil CECe ($cmol_{(c)}\ kg^{-1}$) was calculated based on the sum of the extracted exchangeable cations, and %BS was calculated based on the ratio of the sum of Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} to CECe. After extraction of exchangeable cations, soils were washed three times with 50 mL of double deionized water and extracted with 2 *M* KCl through Whatman 42 filter papers to displace soil-retained ammonium (NH_4^{+}). Total CEC ($cmol_{(c)}\ kg^{-1}$ dry soil) was calculated based on NH_4^{+} concentration in the KCl extract, analyzed colorimetrically by reaction with alkaline phenol and hypochlorite using a SmartChem 200 auto-analyzer (Westco Scientific Instruments Inc., Brookfield, CT) in accordance with SmartChem standard methods (Westco Scientific Instruments Inc., 2007).

3.5 Quantification of Soil Carbon, Nitrogen and Sulphur

Prior to analysis of soil C, N and S, soils were sieved, ground, and oven dried at 60°C for 24 h to remove residual moisture. Percentage TC and TN were analyzed via combustion at 1100°C using a CNS-2000 Elemental Analyzer (Leco Corporation, St. Joseph, Missouri USA). Percentage TOC was analyzed via combustion at 840°C (Wang and Anderson, 1998) using the C 632 Carbon Determinator (Leco Corporation, St. Joseph, Missouri USA). Percentage soil TS was also analyzed via combustion at 1350°C using a Leco SC144DR C/S Analyzer (Leco Corporation, St. Joseph, Missouri USA).

3.6 Quantification of Soil Organic Matter Fractions

3.6.1 Soil microbial biomass

Homogenous sub-samples of surface soil from the north and south transects were isolated for chloroform fumigation and subsequent microbial biomass carbon (MB-C) and microbial biomass nitrogen (MB-N) measurement (Voroney et al., 2008). Mineral soils were sieved to 5 mm and organic and peaty phase soils were sectioned into pieces approximately 5 mm in diameter (Brake et al., 1999; Friedel et al., 2002). All samples were stored at 4˚C for approximately 15 wks prior to pre-incubation.

Approximately 10 g (field moist) of organic and peaty phase soil samples and 10 g (dry mass basis) of mineral samples were pre-incubated in duplicate in 250 mL glass containers with Parafilm® seal, to maintain soil moisture levels. Mineral soil samples were kept at 50% water holding capacity (WHC) for 12 d to minimize effects from microbial populations associated with living roots (Friedel et al., 2002). The approximate WHC of mineral soils was determined from texture-based pedotransfer functions (Pachepsky et al., 2006; Saxton and Rawls, 2006; Al Majou et al., 2008) and approximate bulk densities based on values from reviewed research (Chen et al., 1998). The sample textures were estimated from soil classification and texture data from the 2008 Soil Survey of the Flin Flon - Creighton area (unpublished data), as particle size data from the current study was not available at the time microbial biomass analysis was performed.

After pre-incubation, fumigation treatment was carried out on one replicate of each sample, using ethanol-free chloroform ($CHCl_3$) with a vacuum pump and desiccator system (Voroney et al., 2008). Extraction of unfumigated control samples occurred at time of fumigation, and fumigated samples were extracted after a 24-h incubation period. All samples were extracted with 0.5 *M* K_2SO_4 at a 1:2 soil (g dry mass basis) to extractant solution (mL) ratio, after 1 h agitation on a reciprocating shaker at 175 rpm. Soil suspensions were filtered through Whatman GF 934-AH filter paper and stored at -20˚C prior to analysis. Carbon and N in solution was analyzed via wet oxidation using a TOC analyzer (TOC-V CPH/CPN, Shimadzu Corporation, Kyoto Japan). Microbial biomass C and N was calculated as the difference in C and N extracted from fumigated and unfumigated soils (Voroney et al., 2008).

3.6.2 Water extractable organic carbon and total dissolved nitrogen

Homogenous sub-samples of surface and sub-surface transect soil samples were isolated for extraction of WEOC and TDN. Organic samples were sectioned into unsieved portions, approximately 5 mm in diameter, and mineral samples were sieved to 2 mm. All samples were stored at 4˚C for 6 d prior to extraction. Soil weights were adjusted to 10 g and 5 g (dry mass basis) for mineral and organic soils, respectively (Chantigny et al., 2008). Mineral samples were extracted with a 5 m*M* $CaCl_2$ solution at a 1:2 soil (g dry soil basis) to solution (mL) ratio. Organic samples were extracted with deionized water in the same way, to maintain a 1:10 ratio of soil (g) to water (mL). Mineral samples were agitated for 1 min and left to stand for 4 min before extraction and organic samples were agitated for one min and then left to stand for 24 h with additional agitation occurring three times before extraction. All samples were extracted using 0.45 μm syringe filters and stored at -20˚C prior to analysis. Water extractable organic carbon and TDN in solution were measured via wet combustion-oxidation (WEOC) and thermal decomposition (TDN) using a TOC/TN analyzer (TOC-V CPH/CPN and TNM-1, Shimadzu Corporation, Kyoto Japan).

3.6.3 Density fractionation

Density fractionation of samples was carried out according to Gregorich and Beare (2008) to isolate the LF and HF SOM. Fractions were separated from sub-samples (25 g dry mass basis) of each 0- to 5-cm soil sample with 50 mL of sodium iodide (NaI, specific gravity of 1.55) after shaking for 60 min and then standing untouched for 48 h. The LF (density < 1.55) was aspirated and filtered using vacuum filtration and 0.45 μm Millipore filters; NaI was subsequently rinsed from the LF using 0.01 *M* $CaCl_2$ and distilled water. The remaining HF (density > 1.55) was also rinsed three times under vacuum with 0.01 *M* $CaCl_2$, followed by distilled water. Fractions were dried at 60°C for 12 h and analyzed for total C and N via combustion with a C-N-S analyzer (CNS-2000 Elemental Analyzer, Leco Corporation, St. Joseph, MO USA). Light fraction weight (LF-Wt) was also measured as a percentage of total sample dry weight.

3.7 Statistical Analyses

3.7.1 General statistics

Descriptive statistics, boxplots, and assessment of dataset similarity were carried out using PASW Statistics 18.0 (SPSS, IBM Corporation). The similarity of categories – mineral and organic samples, surface and sub-surface samples, transect samples – was assessed based on data distribution and medians using the Kruskal-Wallis analysis of distribution and the median test of independent samples. The categories were the same if there was no significant difference between both the distributions and medians of categories ($P \leq 0.05$).

3.7.2 Non-metric multidimensional scaling and ordination

To satisfy objective one, interpretation of data patterns for the transects was carried out via non-metric multidimensional scaling (NMDS) using the vegan package (Oksanen et al., 2010) in R (R Development Core Team, 2009), as per Oksanen (2011). Non-metric multidimensional scaling was performed on combined transect data, separated based on sample depth and soil classification (total of four ordinations). The statistical analyses were carried out on untransformed data and utilized a previous best start configuration with a maximum iteration of 100 to avoid local minima (i.e., avoid an ordination that is not the best possible, but the best in comparison to other results achieved). Points, representing samples at a specific sampling location, were plotted on the ordination using a Euclidean distance metric. The number of axes was selected based on a resulting acceptable stress (goodness of fit) level (Kruskal, 1964) of less than 10%, and the ordination was rotated so the first axis represented the highest amount of variation (Oksanen, 2011). A Shepard diagram was created to evaluate goodness of fit between ordination distances versus the dissimilarity of samples, using non-metric and linear regression (ordinations with $r^2 > 0.90$ were accepted). Finally, vectors representing analyzed variables were fit to the ordination and vector significance (p) was evaluated based on 999 random permutations of the data, to ensure results were more non-random (McCune and Grace, 2002; Oksanen, 2011). Vectors with a significance of $P \leq 0.05$ were plotted on the ordination and used to interpret the relationship of variables with transect sampling points.

In addition, Spearman's rank correlation coefficient (Spearman's rho) was employed to evaluate bivariate relationships between analyzed variables and distance

from the smelter, percentage ground species cover and percentage woody species cover, as well as relationships between all variables. Correlation coefficients (r) and significance values (p) were obtained using PASW Statistics 18.0 (SPSS, IBM Corporation) and r values with a $P \leq 0.05$ was identified as significant.

3.7.3 Interpreting ordinations and vectors

Ordinations are well suited for identifying patterns of intercorrelated, multivariate data and are based on the structure of the data itself, instead of an external scale. Due to the interpretive nature of ordinations, scales of axes are without units and are used to identify the spatial coordinates of points and variables within the ordination, instead of a measurement value (Shaw, 2003). These coordinates are based on a defined distance metric (i.e., Euclidean) and determined by ranking data according to dissimilarity between samples–not magnitude of difference. Therefore a successful ordination depicts monotonic relationships between sample dissimilarity and ordination distance, such that similar points in the ordination are in closer proximity to one another in comparison to points that are less similar (Fasham, 1977). Often these groups of similar points are subjectively identified as "clusters" (Shaw, 2003).

Although the significance and variance of an ordination cannot be extracted during analysis, the ordination can be rotated so the first axis encompass the largest amount of variance; the second axis encompass the next largest amount, and so on (Oksanen, 2011). Multiple axes can be selected for the ordination; however, the ability to effectively portray the ordination on paper is diminished with the use of more than two, therefore the first and second axes of a multi-axes model are usually portrayed and interpreted. This being said, the complexity of the data may not lend itself to a two or three axes model and therefore the goodness of fit – or stress – of the ordination should be compared with an increasing number of axes. McCune and Grace (2002) summarize suggested stress levels based on Kruskal (1964) and Clarke and Ainsworth (1993), and suggest stress between 10% and 20% is common for studies of ecological communities. In general, a low stress value reflects a successful portrayal of the relationship between sample dissimilarity and distance in the ordination (Fasham, 1977).

Fitting vectors of environmental variables onto ordination plots help identify how the points on the ordination vary with respect to the variables considered. Oksanen (2011)

identified two main interpretation measures when considering vectors in ordination using the vegan package in R: 1) the direction in which the arrow points, which represents the direction of gradient; and 2) the length of vector, which gives an indication of the correlation between the variable and the ordination. The value of the variables for points within the ordination can be compared by identifying where they lie within the direction of gradient or, in other words, identifying where they lie along the vector. Points lying in opposite direction of where the arrow is pointing (i.e., on the opposite side of the origin from the vector) would have low values of the variable represented by that vector. Conversely, points plotted along the vector would grow in value towards the end (arrow) of the vector, and points at the end of the vector would have the largest values of the variable represented. In addition, if an arrow points to a cluster, the points within the cluster are strongly influenced by (i.e., have high values of) the variable represented by that vector (Shaw, 2003).

The correlation between the ordination and variables represented by the vectors can be inferred from the length of the vector, which is proportional to the r^2 of the environmental variable and the ordination (McCune and Grace, 2002; Oksanen, 2011). In R, vector plotting functions give both the r^2 of the vector with the ordination, as well as a significance (p) value based on randomized permutations of the data (Oksanen, 2011). This allows interpretation of vector significance as well as correlation to the ordination. In addition, the angles and direction of vectors can identify variables that are in close relation with one another (McCune and Grace, 2002), meaning vectors in close proximity (small angles) would be more closely related than those existing at a wider proximity (wider angles). Identifying these relationships can further facilitate interpretation of ordination points plotted within the space of those vector angles.

3.8 Directional Effects

To satisfy objective two, comparisons of the distribution and median of variables between grids was done, as described in Section 3.7.1. Due to the varying number of mineral and organic samples within each grid, the variables were standardized based on soil TOC content prior to statistical analyses. The distribution and median of variable data between grids was compared prior to and after standardization to ensure TOC was

the influential factor on those variables. Variables that were different ($P \leq 0.05$) between grids after standardization were summarized based on grid direction.

4. RESULTS

4.1 Exploring Variability of Vegetation and Soil Parameters Along the North and South Transects

4.1.1 Soil classification and percentage plant cover

The most common soil orders identified at transect sample locations were Regosol, Brunisol, Organic and Gleysol (Soil Classification Working Group, 1998). Details on soil classification of transect pits can be found in Table A.1 in Appendix A. In addition, 10 pits from both transects had a peaty-phase upper horizon but were classified under mineral soil orders (generally Regosolic). Approximately 75% of surface samples, and 80% of sub-surface samples from each transect contained < 17% TOC and were therefore classified as mineral samples; the remaining samples were classified as organic (> 17% TOC). Typical soil parent materials were of till, lacustrine, fluvial or organic origin and the texture class of mineral samples ranged from silty-clay-loam to sandy-loam. The median pH of mineral and organic samples (4.6 and 5.5, respectively) was the same for the north and south transects for both sample depths.

There was no significant ($P \leq 0.05$) difference in percentage ground or woody species cover between transects, according to the Kruskal-Wallis analysis of distribution and the median test of independent samples. Percentage ground species cover was however, different between mineral and organic surface soils and both ground and woody species cover were different between mineral and organic sub-surface samples. The median, minimum and maximum of percentage ground species and woody species cover at transect sample points is summarized based on the mineral or organic classification of the surface soil sample (Table 4.1). Significant differences (Kruskal-Wallis analysis of distribution and the median test of independent samples; $P \leq 0.05$) in plant cover are not identified within the table due to the complexity of the data. Approximately two-thirds of the sample points had less than 50% ground species cover and/or less than 50% woody species cover, although both low ground cover and low woody cover did not always occur simultaneously at the same points. Sixteen points had a ground species cover of 1% or less, and 20 points had a woody species cover of 1% or less. Conversely, 15 sample points had ground species cover of 80% or greater, and five points had 80% woody cover

(the maximum woody cover measured). Fig. 4.1 displays images of point S.Tr.01 with 0% (low) (Fig. 4.1a), and point N.Tr.01 with 80% (high) ground species cover (Fig. 4.1b). Fig. 4.2. displays images of point with 0% (low) woody species cover (Fig 4.2a) and 80% (high) woody species (Fig. 4.2b). Typical ground cover species identified included a variety of grasses (*Poaceae spp.* and *Gramineae spp.*), sedges (*Carex spp.)*, mosses and lichens, as well as (to a lesser extent) various shrubs, including Labrador tea (*Ledum groenlandicum*), bearberry (*Arctostaphylos uva-ursi*) and wild rose (*Rosa acicularis*). Typical species identified in woody cover estimation included white birch (*Betula papyrifera* var. *papyrifera*), black spruce (*Picea mariana*), white spruce (*Picea glauca*), jack pine (*Pinus banksiana*), trembling aspen (*Populus tremuloides*), as well as red-osier dogwood (*Cornus stolonifera*), several varieties of willow (*Salix spp.*), and alder (*Alnus rugosa*).

Table 4.1. Median (Med), minimum (Min) and maximum (Max) values of percentage ground species and percentage woody species cover for north and south transect sampling points. Data are separated based on mineral (< 17% TOC) or organic (> 17% TOC) classification of the surface (0- to 5-cm) soil samples.

Sample	Ground Species Cover			Woody Species Cover		
	Min.	Med.	Max.	Min.	Med	Max
	--- % ---					
North Transect						
Mineral (n = 23)	0	10	80	0	40	80
Organic (n = 8)	20	80	80	0	10.5	80
South Transect						
Mineral (n = 23)	0	20	90	0	10	80
Organic (n = 8)	30	80	90	10	30	80

† Explanation of significant differences (Kruskal-Wallis analysis of distribution and the median test of independent samples; $P \leq 0.05$) in percentage ground species or woody species cover can be found in section 4.1.1, and are not identified in the table due to complexity of data structure.

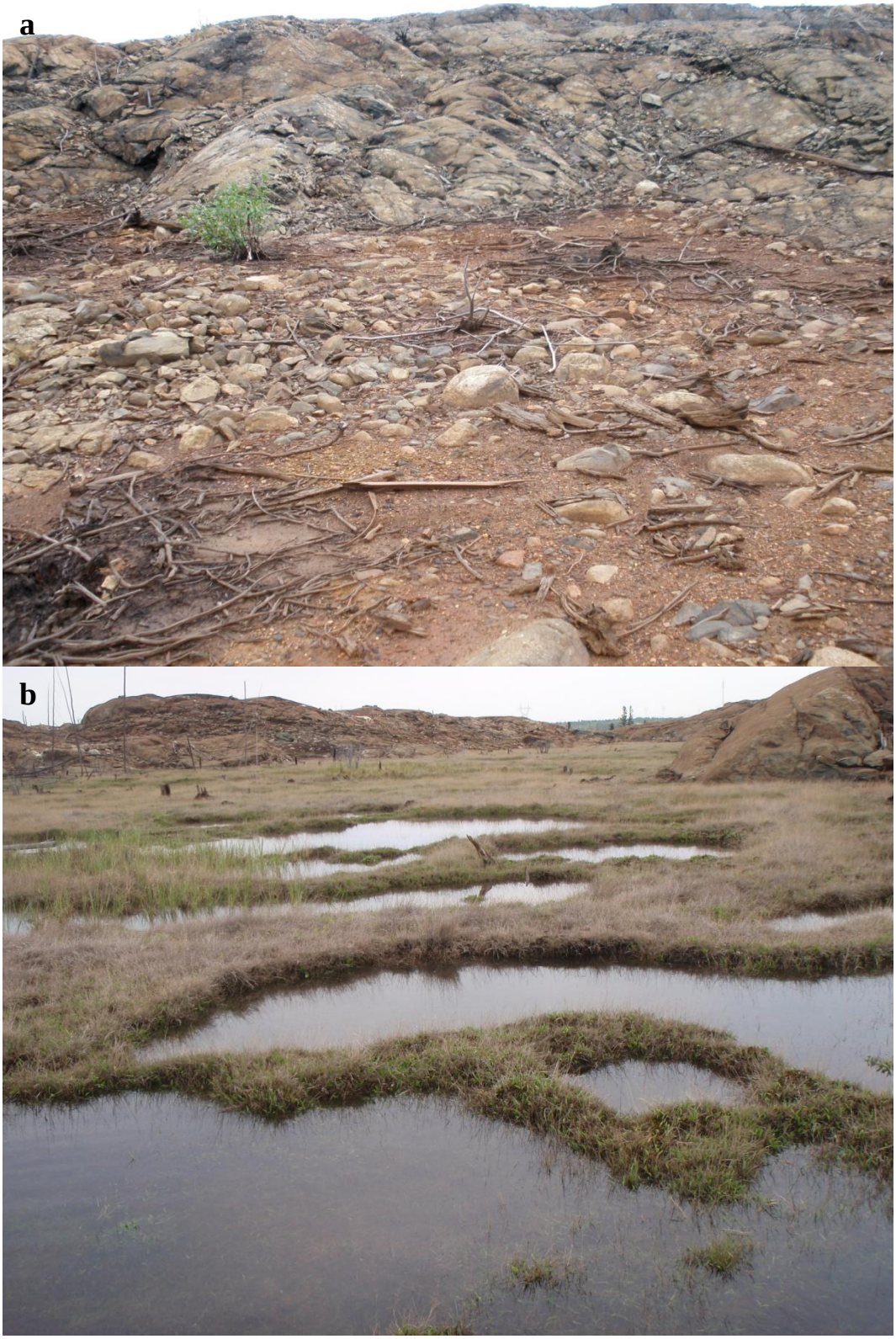

Fig. 4.1. Photos from the Flin Flon-Creighton transects of point S.Tr.04 with low (0%) ground species cover, 0.4-km along the south transect (a); and point N.Tr.01 with high (80%) ground species cover, 0.1-km along the north transect (b).

Fig. 4.2. Photos from the Flin Flon-Creighton transects of point N.Tr.04 with low (0%) woody species cover, 0.4-km along the north transect (a); and point N.Tr.30 with high (80%) woody species cover, 3-km along the north transect (b).

4.1.2 Soil organic matter fractions

The distribution of LF and HF SOM characteristics for transect samples, based on mineral or organic classification, are displayed in Figs. 4.3 to 4.5; the mean and standard deviation of LF and HF characteristics are summarized in Tables A.2 to A.5 in Appendix A. Within the north transect, LF-Wt (Fig. 4.3), LF- and HF-C (Fig. 4.4), and LF- and HF-N (Fig. 4.5) were higher ($P \leq 0.05$) in organic samples compared to mineral, but the LF- and HF-C:N ratios between mineral and organic soils were statistically the same ($P \leq 0.05$; LF = ~ 30 - 45; HF = ~20 - 30) (HF-C:N of mineral and organic samples had different distribution but the same median). Within the south transect, LF-Wt (Fig. 4.3), LF- and HF-C (Fig. 4.4), and HF-N (Fig. 4.5) were also higher ($P \leq 0.05$) in organic samples compared to mineral; however, LF-N (median = ~ 1% N) and LF- and HF-C:N (LF = ~ 30; HF = ~ 20) were not statistically different ($P \leq 0.05$) between classifications. When comparing between transects, based on mineral or organic soil classification, all variables were statistically similar ($P \leq 0.05$) except for the LF-Wt, LF-N and LF-C:N of mineral samples. South transect mineral samples, in comparison to north transect mineral samples, had a wider distribution of LF-Wt (but similar medians; Fig. 4.3), and higher LF-N content (median = 1.15% N in south transect *vs.* 0.77% N in north transect mineral samples) and lower LF-C:N (median = 31.6 in south transect *vs.* 45.8 in north transect mineral samples).

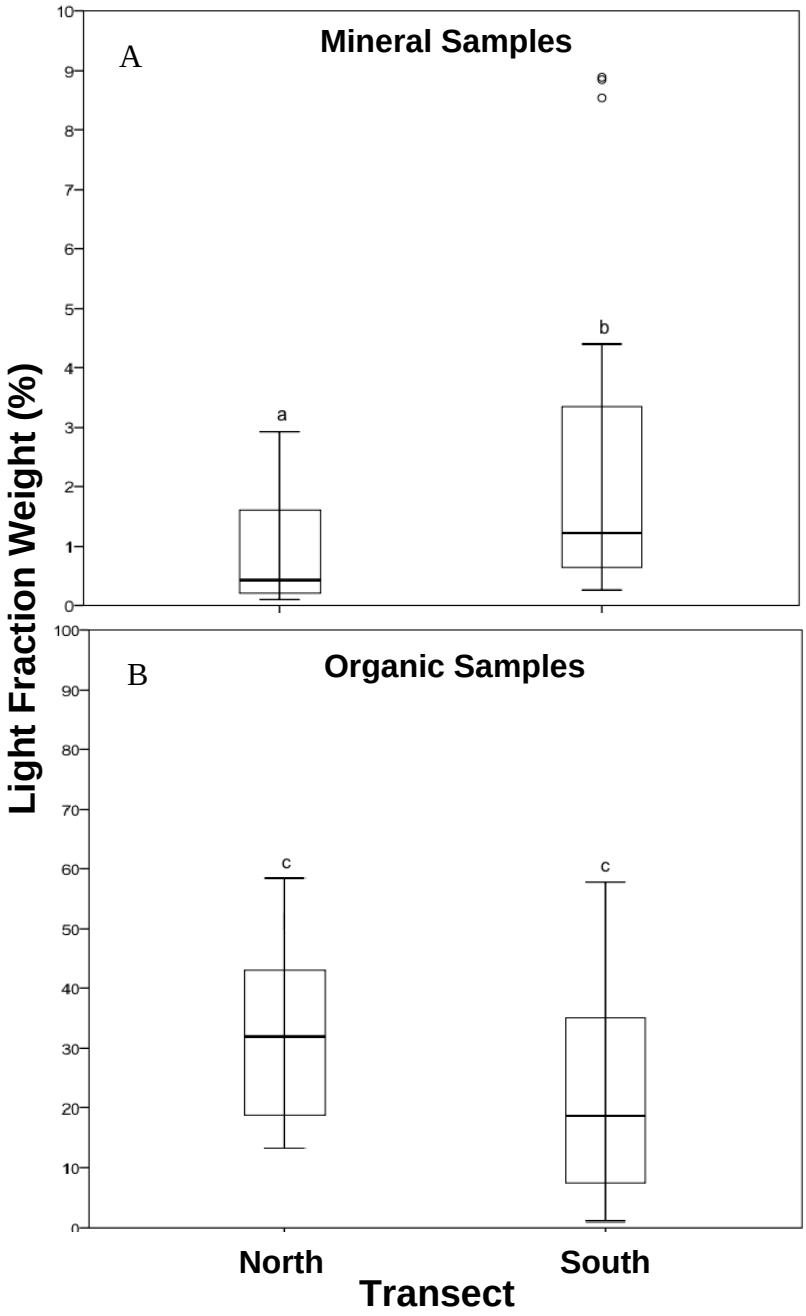

Fig. 4.3. Comparison of light fraction (LF) weight (as a percentage of total soil dry weight) distribution between north and south transects, based on (a) mineral (< 17% TOC) or (b) organic (> 17% TOC) (b) classification of surface (0- to 5-cm) soil samples. Note the different scales for LF-Wt % for each sample classification. The data median (central tendency lines), 1st and 3rd quartiles (bottom and top of box) and minimum and maximum (bottom and top of whiskers) are displayed. Circles identify outliers lying between 1.5 and 3 times the interquartile range. An extreme outlier (beyond 3 times the interquartile range) was removed from boxplot for the south transect mineral sample distribution at 43.68%. Differences in variables based on classification (mineral or organic) or transects are indicated with letters above the boxplot of the respective sample group (Kruskal-Wallis analysis of distribution and the median test of independent samples; $P \leq 0.05$).

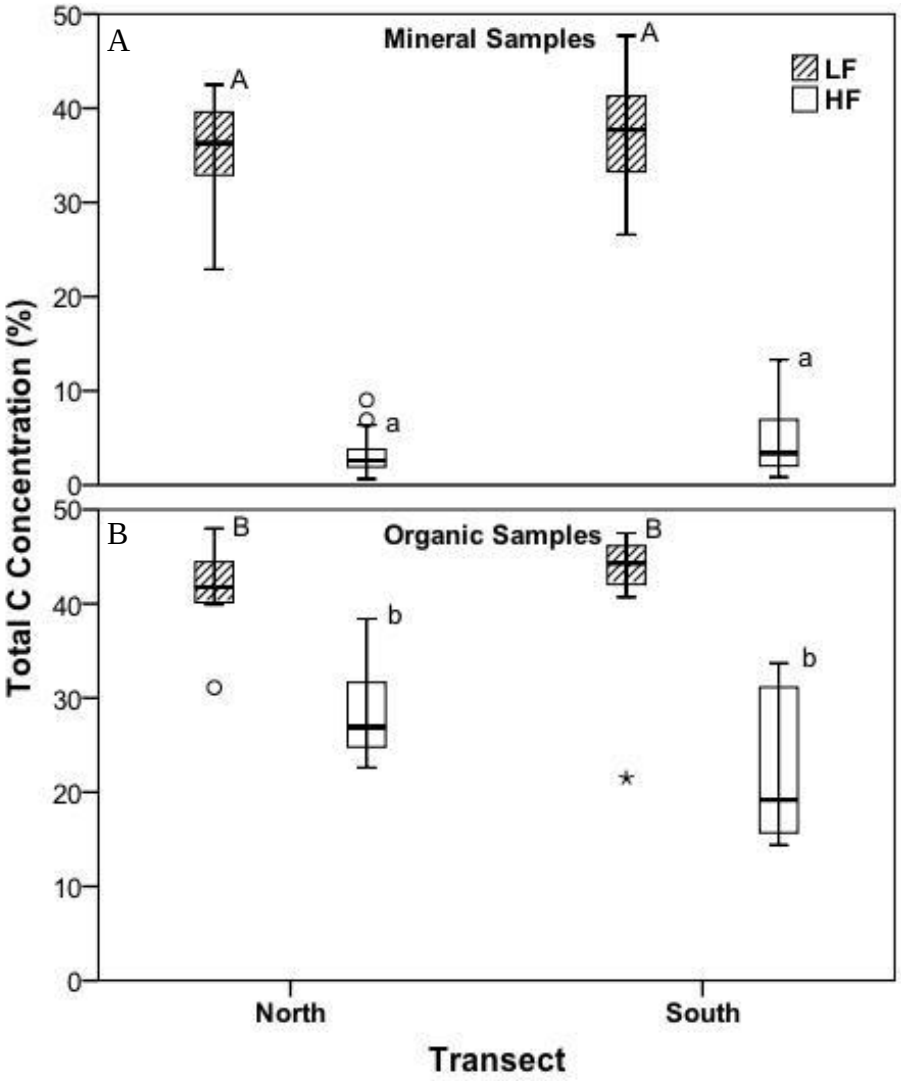

Fig. 4.4. Comparison of total carbon concentration (%) in light fraction (LF) and heavy fraction (HF) SOM, based on mineral (< 17% TOC) or organic (> 17% TOC) classification of north and south transect surface (0- to 5-cm) soil samples. The data median (central tendency line), 1st and 3rd quartiles (bottom and top of box) and minimum and maximum (bottom and top of whiskers) are displayed. Circles identify outliers lying between 1.5 and 3 times the interquartile range; stars identify extreme outliers lying beyond 3 times the interquartile range. Differences in variables based on classification (mineral or organic) or transects are indicated with letters (uppercase = classification; lowercase = transect) above the boxplot of the respective sample group (Kruskal-Wallis analysis of distribution and the median test of independent samples; $P \leq 0.05$).

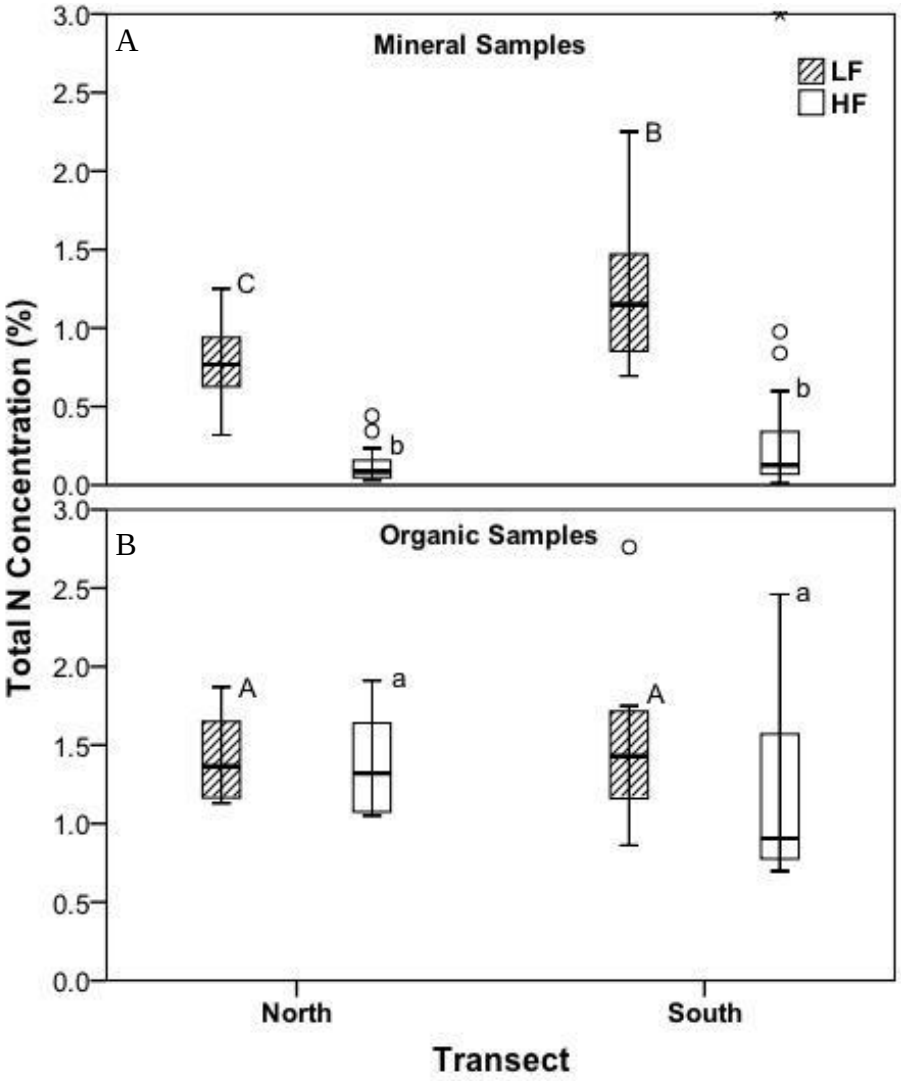

Fig. 4.5. Comparison of total nitrogen concentration (%) in light fraction (LF) and heavy fraction (HF) SOM, based on mineral (< 17% TOC) or organic (> 17% TOC) classification of north and south transect surface (0- to 5-cm) soil samples. The data median (central tendency line), 1st and 3rd quartiles (bottom and top of box) and minimum and maximum (bottom and top of whiskers) are displayed. Circles identify outliers lying between 1.5 and 3 times the interquartile range; stars identify extreme outliers lying beyond 3 times the interquartile range. Differences in variables based on classification (mineral or organic) or transects are indicated with letters (uppercase = classification; lowercase = transect) above the boxplot of the respective sample group (Kruskal-Wallis analysis of distribution and the median test of independent samples; $P \leq 0.05$).

The distribution of WEOC and TDN for both transects are displayed in Figs. 4.6 and 4.7 and the mean and standard deviation of WEOC and TDN data are summarized in Tables A.2 to A.5 in Appendix A. For both transects, WEOC (Fig. 4.6) and TDN (Fig.

4.2) content were not significantly different in surface *vs.* sub-surface samples, but differed based on mineral or organic classification of samples (excluding TDN in north transect surface samples, which had statistically similar medians but different distribution). When comparing between transects, WEOC and TDN content (both sample depths) were not significantly different based on mineral or organic classification of soil samples. The median WEOC of surface mineral samples was 2.23 mg C kg^{-1} soil and 3.08 mg C kg^{-1} soil for the north and south transects, respectively, compared to 22.77 mg C kg^{-1} soil and 38.97 mg C kg^{-1} soil for the organic soils from the north and south transects, respectively (similar values were obtained for sub-surface samples from each soil classification, for each transect). The median TDN of surface mineral samples was 0.51 mg N kg^{-1} soil for both the north and south transects, compared to 4.43 mg N kg^{-1} soil and 2.65 mg N kg^{-1} soil for organic surface samples for the north and south transects, respectively. Again, similar values were obtained for sub-surface samples.

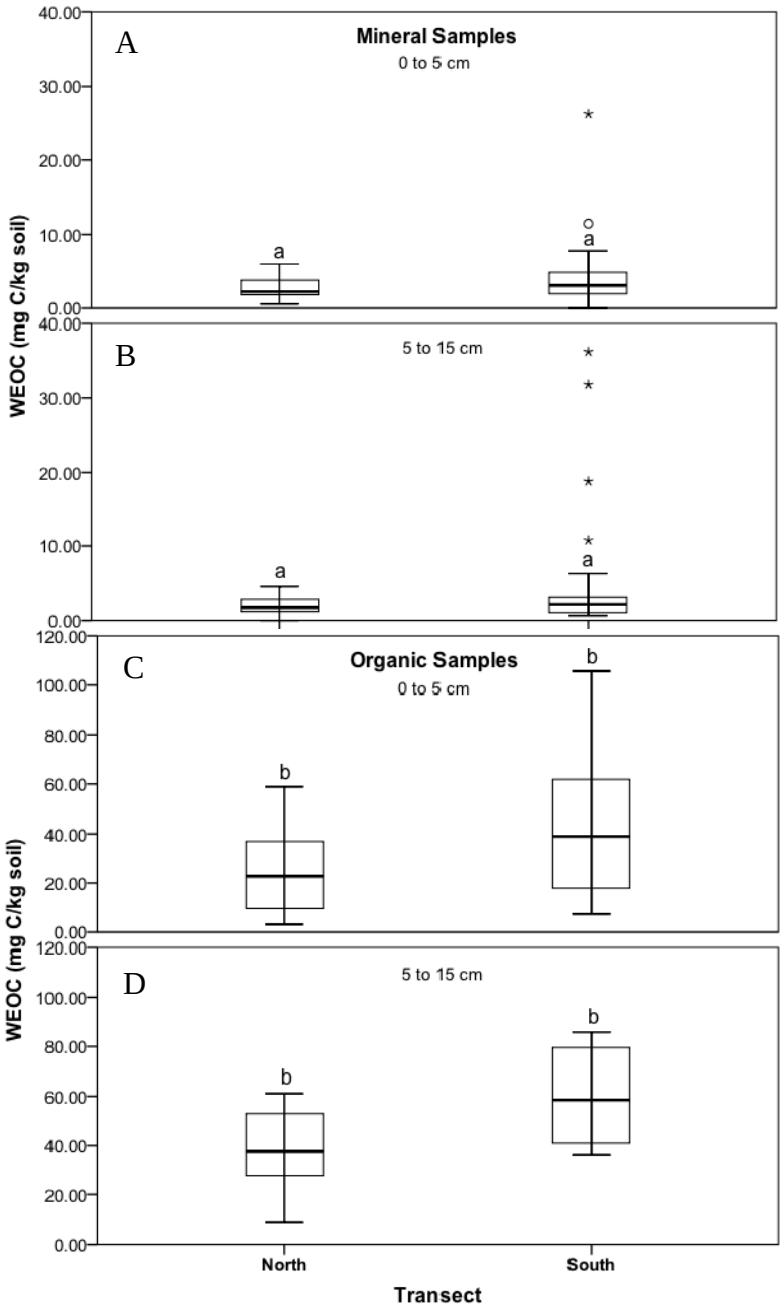

Fig. 4.6. Comparison of water extractable organic carbon (WEOC) (mg C kg^{-1} soil) between north and south transects, based on (A, B) mineral (< 17% TOC) or (C, D) organic (> 17% TOC) classification of (A, C) surface (0- to 5-cm) and (B, D) sub-surface (5- to 15-cm) soil samples. Note that the scales are not the same for mineral and organic sample boxplots. The data median (central tendency lines), 1st and 3rd quartiles (bottom and top of box) and minimum and maximum (bottom and top of whiskers) are identified. Stars identify extreme outliers lying beyond 3 times the interquartile range. Letters above the boxplot identify significant differences based on classification, sample depth or transect when comparing all datasets (Kruskal-Wallis analysis of distribution and the median test of independent samples; $P \leq 0.05$).

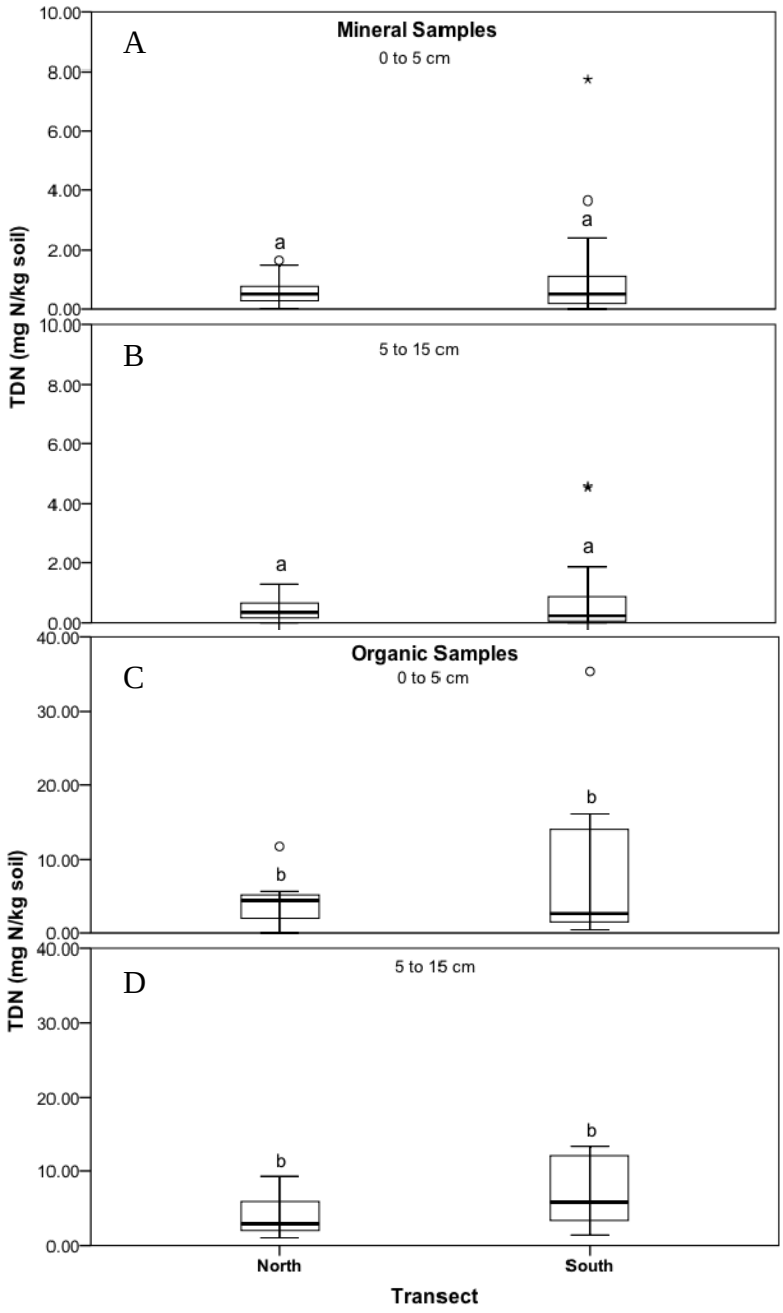

Fig. 4.7. Comparison of total dissolved nitrogen (TDN) (mg N kg^{-1} soil) between north and south transects, based on (A, B) mineral (< 17% TOC) or (C, D) organic (> 17% TOC) classification of (A, C) surface (0- to 5-cm) and (B, D) sub-surface (5- to 15-cm) soil samples. Note that the scales are not the same for mineral and organic sample boxplots. The data median (central tendency lines), 1st and 3rd quartiles (bottom and top of box) and minimum and maximum (bottom and top of whiskers) are identified. Circles identify outliers lying between 1.5 and 3 times the interquartile range; stars identify extreme outliers lying beyond 3 times the interquartile range. Letters above the boxplot identify significant differences based on classification, sample depth or transect when comparing all datasets (Kruskal-Wallis analysis of distribution and the median test of independent samples; $P \leq 0.05$).

Analysis of MB yielded negative values (data not displayed). This may have been due to a high concentration of charcoal in samples (based on visual observation), which can adsorb fresh microbial-derived organic C and N present after fumigation treatment (Durenkamp et al., 2010; Liang et al., 2010). The majority of negative results occurred with MB-N in organic samples from the north transect; however, due to the variability of charcoal content in all samples and assumed variability of MB measurement accuracy, results were removed from any further statistical analyses.

4.1.3 Soil carbon, nitrogen and sulphur

Medians, minima and maxima of whole soil sample TOC, TN, C:N, and TS are summarized in Table 4.2 by sample depth, soil classification and transect. The mean and standard deviation of soil nutrients analyzed in transect samples are summarized in Tables A.2 to A.5 in Appendix A. Within the north transect, nutrient contents in surface and sub-surface samples were not significantly different ($P \leq 0.05$), considering mineral and organic classification, but organic samples (for both depths) had higher ($P \leq 0.05$) TOC, TN and TS content than mineral samples (Table 4.2). In addition, the soil C:N was statistically similar (21.06 to 26.57, $P \leq 0.05$) for mineral and organic samples (for both depths). Within the south transect, soil C:N and TS content were not significantly different ($P \leq 0.05$) in surface and sub-surface samples, for both mineral and organic samples. The distribution of TOC (both mineral and organic samples) and TN (mineral samples only) were, different between surface and sub-surface samples, whereas median values were statistically similar ($P \leq 0.05$, Table 4.2). When comparing samples based on classification, both depths from the south transect had higher TOC, TN and TS in organic versus mineral soil samples ($P \leq 0.05$, Table 4.2) whereas the soil C:N of mineral and organic soil samples were not significantly different (median = 18.48 to 21.38, $P \leq 0.05$). Each nutrient was statistically similar ($P \leq 0.05$) between transects in both depths of organic samples, as well as in sub-surface mineral samples. Between the transects, TS was higher in south transect samples (south median = 0.07% versus north median = 0.02%), and the distribution of TN and soil C:N were different between transects as well (same median) (Table 4.2) ($P \leq 0.05$). Significant differences (Kruskal-Wallis analysis of distribution and the median test of independent samples; $P \leq 0.05$) in soil nutrient contents are not identified within the table due to the complexity of the data.

Table. 4.2. Median (Med), minimum (Min) and maximum (Max) of soil nutrients in surface (0- to 5-cm) and sub-surface (5- to 15-cm) mineral and organic soil samples for the north and south transects).†

Sample Group	--- TOC‡ ---			--- TN§ ---			--- C:N¶ ---			--- TS# ---		
	Med	Min	Max	Med	Min	Max	Med	Min	Max	Med	Min	Max
	---- % ----											
North Transect												
Mineral												
Surface	2.97	0.53	7.97	0.14	0.04	0.44	26.57	13.65	51.50	0.02	0.01	0.15
Sub-surface	1.89	0.24	8.54	0.10	0.02	0.54	21.06	5.02	79.50	0.02	0.01	0.08
Organic												
Surface	41.31	30.66	47.70	1.88	1.40	2.25	21.50	17.05	33.86	0.32	0.20	0.73
Sub-surface	46.56	35.94	47.26	1.90	1.38	2.50	23.73	18.32	33.70	0.37	0.24	0.91
South Transect												
Mineral												
Surface	3.22	0.80	15.30	0.20	0.05	1.13	18.55	12.04	30.43	0.07	0.01	4.50
Sub-surface	1.77	0.03	11.69	0.10	0.04	0.57	18.48	10.36	27.72	0.03	0.01	0.45
Organic												
Surface	33.70	19.20	44.93	1.51	0.89	3.03	19.18	14.65	30.78	0.48	0.06	0.92
Sub-surfaces	46.24	38.99	48.81	2.03	0.94	2.36	21.38	11.83	39.73	0.58	0.18	4.23

† Explanation of significant differences (Kruskal-Wallis analysis of distribution and the median test of independent samples; $P \leq 0.05$) in soil nutrients can be found in the section 4.1.3, and are not identified in the table due to complexity of data structure.

‡ TOC = total organic carbon

§ TN = total nitrogen

¶ C:N = soil carbon to nitrogen ratio

TS = total sulphur

4.1.4 Additional soil characteristics

The median, minimum and maximum values for total CEC, CECe and %BS, organized by depth, transect and soil sample classification, are displayed in Table 4.3. The mean and standard deviation of total CEC, CECe and %BS analyzed in transect samples are presented in Table A.2 to A.5 in Appendix A. Within the north transect, total CEC, CECe and %BS of surface and sub-surface samples were significantly different ($P \leq 0.05$) based on mineral and organic classification, whereas all variables were the statistically similar between mineral or organic classification, except the CECe of organic sub-surface samples (median = 7.29 $cmol_{(c)}$ kg^{-1} soil) was higher ($P \leq 0.05$) than mineral sub-surface samples (median = 3.75 $cmol_{(c)}$ kg^{-1} soil). Within the south transect, there was no significant difference ($P \leq 0.05$) in total CEC, CECe and %BS between sample depth or mineral or organic sample classification. When comparing between transects, each variable was statistically similar between sample depths for organic samples; however, %BS in north transect surface mineral samples was higher than in south transect surface mineral samples and the CECe of south transect mineral sub-surface samples was higher than north transect mineral samples from the same depth ($P \leq 0.05$, Table 4.3). Significant differences (Kruskal-Wallis analysis of distribution and the median test of independent samples; $P \leq 0.05$) in total CEC, CECe and %BS are not identified within the table due to the complexity of the data.

Table 4.3. Median (Med), minimum (Min) and maximum (Max) of total cation exchange capacity (CEC), effective cation exchange capacity (CECe) and percent base saturation (%BS) for surface (0- to 5-cm) and sub-surface (5- to 15-cm) mineral and organic transect samples. †

Sample Group	--- Total CEC ---			--- CECe ---			--- %BS ---		
	Med	Min	Max	Med	Min	Max	Med	Min	Max
	---- $cmol_{(c)}$ kg^{-1} soil ----						--- % ---		
North Transect									
Mineral									
Surface	10.36	4.77	38.14	5.04	0.83	56.50	89.76	8.92	100.00
Sub-surface	11.16	2.16	73.90	3.75	0.59	82.14	82.29	5.76	100.00
Organic									
Surface	8.76	6.12	43.67	8.91	2.10	77.15	89.63	14.32	100.00
Sub-surface	9.49	3.17	42.73	7.29	5.40	51.60	53.60	8.11	100.00
South Transect									
Mineral									
Surface	6.78	1.71	37.26	7.04	3.16	80.35	37.43	4.63	99.88
Sub-surface	5.33	1.27	46.33	6.27	2.40	68.18	55.70	3.59	99.97
Organic									
Surface	9.41	2.79	23.22	9.98	3.72	62.61	55.57	6.54	99.74
Sub-surface	7.72	1.72	34.94	7.15	2.36	43.36	24.38	6.63	98.03

† Explanation of significant differences (Kruskal-Wallis analysis of distribution and the median test of independent samples; $P \leq 0.05$) in total CEC, CECe and %BS can be found in section 4.1.4, and are not identified in the table due to complexity of data structure.

The median, minimum and maximum values for individual cations are displayed in Table 4.4; the mean and standard deviation of exchangeable cations analyzed in transect samples are in Tables A.2 to A.5 in Appendix A. Within the north and south transects individually, the cation concentrations did not differ with depth, nor based on mineral or organic sample classification ($P \leq 0.05$). Between transects, there were no significant differences ($P \leq 0.05$) in the contents of cations in organic samples but between mineral samples, Al^{3+} was higher in both depths of south transect mineral samples (median: surface = 2.92 $cmol_{(c)}$ Al^{3+} kg^{-1} soil; sub-surface = 1.95 $cmol_{(c)}$ Al^{3+} kg^{-1} soil), versus north transect mineral samples (median: surface = 0.34 $cmol_{(c)}$ Al^{3+} kg^{-1} soil; sub-surface = 0.26 $cmol_{(c)}$ Al^{3+} kg^{-1} soil) ($P \leq 0.05$). Calcium had the widest range and highest values of all cations analyzed, followed by Al^{3+} and Mg^{2+} (Table 4.4). Sodium and K^{+} were negligible in most of the samples analyzed. Significant differences (Kruskal-Wallis analysis of distribution and the median test of independent samples; $P \leq 0.05$) in cations are not identified within the table due to the complexity of the data.

Table 4.4. Median (Med), minimum (Min) and maximum (Max) of exchangeable cations analyzed in surface (0- to 5-cm) and sub-surface (5- to 15-cm) mineral and organic transect samples.†

Sample Group	--- Ca^{2+} ---			--- Mg^{2+} ---			--- Na^{+} ---			--- K^{+} ---			--- Al^{3+} ---		
	Med.	Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	Med.	Min	Max	Med.	Min	Max
	---- $cmol_{(c)}$ kg^{-1} soil ----														
North Transect															
Mineral															
Surface	2.73	0.20	50.13	0.39	0.00	6.25	0.07	0.00	1.05	0.16	0.08	0.83	0.34 b	0.00	8.60
Sub-surface	1.19	0.08	73.56	0.20	0.00	8.35	0.06	0.00	1.27	0.16	0.00	0.60	0.26 b	0.00	6.56
Organic															
Surface	5.38	0.47	63.27	0.76	0.00	11.50	0.10	0.00	1.70	0.37	0.15	0.56	0.58	0.00	5.34
Sub-surface	2.80	0.38	38.25	0.42	0.00	10.57	0.09	0.00	2.30	0.15	0.10	0.40	3.67	0.00	6.81
South Transect															
Mineral															
Surface	1.21	0.09	76.23	0.51	0.00	5.39	0.07	0.05	1.04	0.23	0.09	1.63	3.92	0.06	7.16
Sub-surface	1.59	0.00	61.57	0.46	0.00	5.83	0.08	0.04	1.35	0.18	0.05	1.05	1.95	0.01	7.69
Organic															
0- to 5-cm	3.53	0.05	55.94	1.02	0.00	8.57	0.12	0.06	0.25	0.27	0.07	1.08	2.92	0.17	7.27
5- to 15-cm	1.02	0.14	40.12	0.62	0.00	3.49	0.10	0.05	0.22	0.14	0.08	0.57	3.13	0.59	6.35

† Explanation of significant differences (Kruskal-Wallis analysis of distribution and the median test of independent samples; $P \leq 0.05$) in cations can be found in the section 4.1.4, and are not identified in the table due to complexity of data structure.

4.2 Evaluation of Variables in Relation to Distance from the Smelter Stack; and Percentage Ground and Woody Species Cover

Mineral Samples

The ordination for north and south transect mineral surface (0- to 5-cm) samples (Fig. 4.8) utilized a three-axes model. The three-axes ordination solution converged after three attempts and resulted in a stress of 6.8%. The Shepard diagram identified a non-metric fit r^2 of 0.995 and a linear fit r^2 of 0.974, indicating a good fit of dataset to the ordination. Vectors representing all variables that had a significance of $P \leq 0.05$ are plotted; r^2 and P values for all variable vectors (for axes one and two, but based on the three axes model) are displayed in Table 4.5. Although several vectors were significant ($P \leq 0.05$) for the surface mineral sample ordination, %BS, percentage woody cover and Al^{3+} had the highest correlation with the ordination (Table 4.5). Vectors grouped according to two themes that ran roughly perpendicular to one another: 1) cation and cation exchange (including %BS and Al^{3+}) which roughly corresponded with axis 1 and therefore encompassed majority of data variance; and 2) SOM quality and quantity, which corresponded to axis 2 and therefore encompassed less data variance as vectors corresponding with axis 1. In addition, distance, percentage ground cover and percentage woody cover vectors ran parallel to (i.e. were related to) several of the SOM vectors, and TS ran between the group of SOM vectors and the Al^{3+} vector (Fig. 4.8).

Among the cation and cation exchange vectors, %BS, Al^{3+} and total CEC were most significantly correlated with the ordination (Table 4.5), though the %BS and Al^{3+} vectors ran in opposite directions (inverse relationship between %BS and Al^{3+}). In addition, the total CEC, CECe, Ca^{2+} and Mg^{2+} vectors all were closely grouped together, and were adjacent to the %BS vector. The distance, percentage ground cover and percentage woody cover vectors ran roughly perpendicular to the cation and cation exchange vectors indicating that, although much of the variance of the ordination was represented by %BS and Al^{3+}, distance and plant cover were more related to SOM vectors (which ran roughly perpendicular to cation and cation exchange vectors).

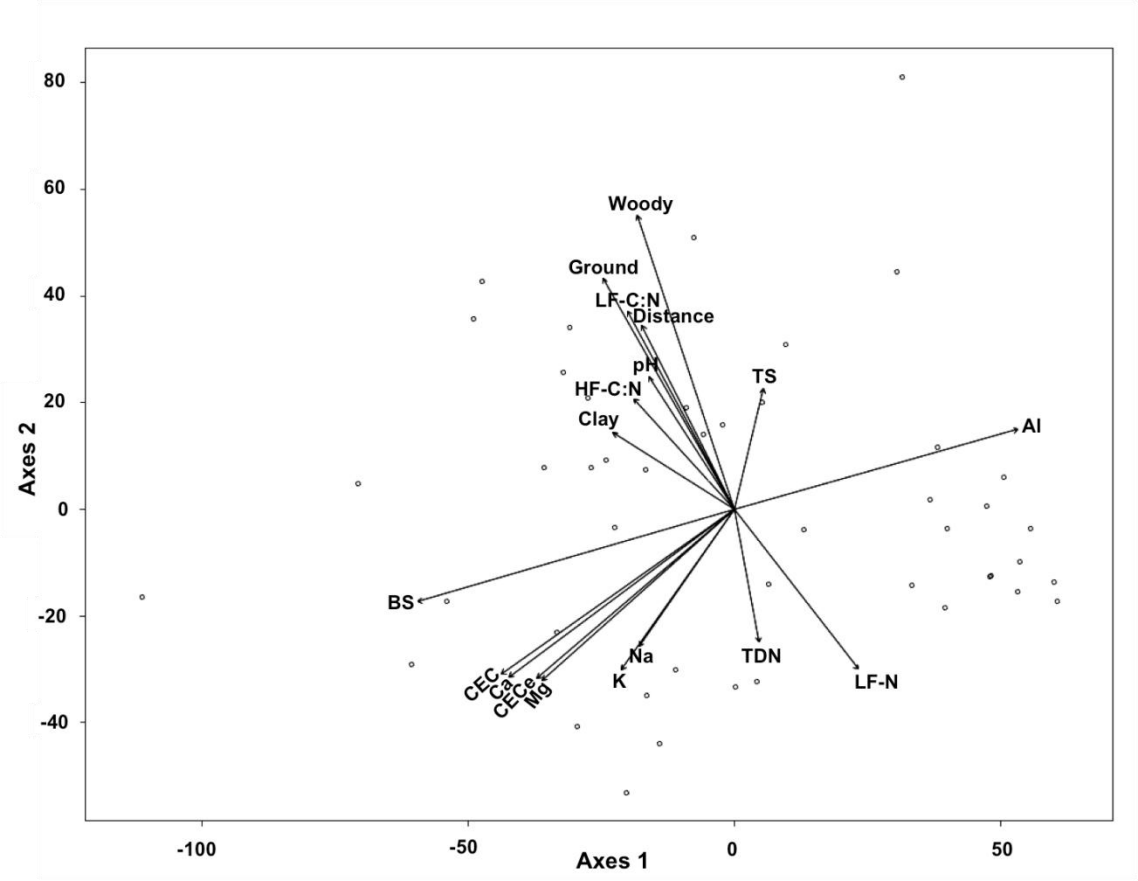

Fig. 4.8. Ordination displaying north and south transect points that had mineral surface (0- to 5-cm) samples, and significant ($P \leq 0.05$) vectors of variables analyzed in those samples. Note: Woody = percentage woody species cover, Ground = percentage ground species cover, LF-C:N = light fraction C:N, Distance = distance from the smelting stack, pH = soil pH, HF-C:N = heavy fraction C:N, TS = total soil sulphur, Clay = percentage clay content, BS = percent base saturation, Al = aluminum, CEC = total cation exchange capacity, Ca = calcium, CECe = effective cation exchange capacity, Mg = magnesium, K = potassium, Na = sodium, TDN = total dissolved nitrogen, LF-N = light fraction nitrogen content.

Table. 4.5. Coefficient of determinations (r^2) and significance (P) values for vectors of variables measured in both the north and south transects mineral and organic, surface (0- to 5-cm) and sub-surface (5- to 15-cm) samples. Vectors significant at P ≤ 0.05 are in bold, the three vectors with the highest r^2 for each sample set are italicized and dashes indicate the variable was not measured for that sample set.

Variable	Mineral Samples				Organic Samples			
	Surface		Sub-surface		Surface		Sub-surface	
	r^2	P	r^2	P	r^2	p	r^2	P
Distance	0.3347	**0.001**	0.3034	**0.001**	0.0878	0.537	0.0279	0.881
Woody Cover	*0.7580*	**0.001**	0.4388	**0.001**	0.6850	**0.002**	*0.9318*	**0.001**
Ground Cover	0.5597	**0.001**	0.7776	**0.001**	0.5346	**0.006**	0.6333	**0.013**
WEOC	0.0166	0.690	0.0879	0.116	0.6629	**0.001**	0.1421	0.497
TDN	0.1450	**0.035**	0.1332	**0.031**	0.5840	**0.002**	0.0186	0.906
LF-Wt	0.0093	0.854	-	-	0.3934	**0.030**	-	-
LF-C	0.0702	0.230	-	-	0.0198	0.879	-	-
LF-N	0.3234	**0.001**	-	-	0.3103	0.091	-	-
LF-C:N	0.4022	**0.001**	-	-	0.3677	0.054	-	-
HF-C	0.0369	0.448	-	-	0.1800	0.281	-	-
HF-N	0.0512	0.326	-	-	0.4066	**0.026**	-	-
HF-C:N	0.1774	**0.023**	-	-	0.1609	0.315	-	-
TOC	0.0253	0.593	0.0025	0.941	0.2684	0.125	0.2832	0.251
TN	0.0394	0.433	$4.1x10^{-5}$	0.999	0.5233	**0.010**	0.1364	0.532
C:N	0.1097	0.083	0.0117	0.771	0.1259	0.421	0.1192	0.569
TS	0.1213	**0.050**	0.0223	0.584	0.3296	0.076	0.1870	0.365
pH	0.1967	**0.009**	0.3277	**0.001**	0.1388	0.381	0.1010	0.631
Total CEC	0.6466	**0.001**	0.7116	**0.001**	0.7115	**0.001**	*0.8012*	**0.001**
CECe	0.5373	**0.001**	0.7591	**0.001**	*0.7600*	**0.001**	0.7264	**0.001**
Ca	0.6284	**0.001**	*0.8072*	**0.001**	*0.8137*	**0.001**	0.7775	**0.001**
Mg	0.5254	**0.001**	*0.7796*	**0.001**	*0.7310*	**0.001**	0.7288	**0.001**
Na	0.2214	**0.002**	0.1920	**0.005**	0.3231	**0.046**	0.5566	**0.027**
K	0.3061	**0.002**	0.4693	**0.001**	0.5809	**0.002**	0.4172	0.077
Al	*0.6880*	**0.001**	0.6520	**0.001**	0.5180	**0.007**	0.6318	**0.016**
%BS	*0.8655*	**0.001**	*0.8208*	**0.001**	0.7179	**0.002**	*0.8820*	**0.001**
%Clay	0.1637	**0.020**	0.1619	**0.018**	-	-	-	-

Among the SOM quality and quantity vectors, LF C:N and LF-N vectors were most significantly correlated with the ordination; however, the ground cover, woody cover and distance vectors were more significantly correlated with the ordination than any of the SOM vectors (Table 4.5). In addition, the TDN and LF-N (SOM quality/quantity) vectors ran parallel to each other and in opposite direction to the other SOM (quality) vectors, which is logical because increasing C:N identifies more C and less N in the SOM pool. The orientation of SOM vectors in relation to distance and percentage plant cover also shows that the C:N of LF and HF increase, and TDN and LF-N content decrease, with distance and plant cover (Fig. 4.8).

Based on the direction of gradients of vectors in relation to plotted points in Fig. 4.8, some trends with regards to distance and plant cover can be extrapolated from the ordination diagram. Generally, points within close proximity to the smelter have low plant cover and low pH, high values of TDN and LF-N, narrower LF and HF C:N. The opposite pattern occurs with increasing plant cover and distance from the smelter. Percent clay appears to be lower nearest the smelter as well; however, the relatively low r^2 value with the ordination suggests this may be the result of interactions of various relationship patterns with other variables. This is further supported by Spearman's rho correlations (Tables A.6 to A.13 in Appendix A), which do not identify any significant ($P \leq 0.05$) relationships between %clay and distance, ground species cover, or woody species cover. Furthermore, although it appears TS increases with distance and plant cover in the ordination, the low r^2 value with the ordination also suggests interacting relationships with other variables. In comparison, Spearman's rho correlations identify significant ($P \leq 0.05$) inverse relationships between TS with distance and woody species cover but positive relationships between TS and several SOM variables (Tables A.6 to A.13 in Appendix A). Points with high values of %BS (and low values of Al^{3+}) have higher cation and cation exchange values, and vice versa; however, these vectors are perpendicular to the distance and plant cover vectors, making trends between cations and cation exchange with distance and ground cover less obvious.

The ordination for north and south transect mineral sub-surface (5- to 15-cm) samples (Fig. 4.9) also utilized a three axes model, and the ordination projection was also created with axes 1 and 2 only. The three-axes ordination solution converged after seven tries and resulted in a stress of 5.7%. The Shepard diagram identified a non-metric fit r^2 of 0.997 and a linear fit r^2 of 0.983, indicating good fit of the dataset to the ordination. Vectors representing all variables that had a significance of $P \leq 0.05$ are plotted; r^2 and P values of all variable vectors (for axes 1 and 2 but based on the three axes model) are displayed in Table 4.5. Several vectors were significant for the sub-surface mineral sample ordination; however, %BS, Ca^{2+} and Mg^{2+} vectors had the highest correlation with the ordination (Fig. 4.9, Table 4.5). The vectors in the sub-surface mineral sample ordination grouped according to three general themes: 1) %BS and Al^{3+} content, which roughly corresponded with axis 1 and therefore encompassed majority of data variance;

2) cation and cation exchange, which also roughly corresponded to axis 1 but did not group closely %BS and Al^{3+}; and 3) distance and percentage plant cover, which corresponded to axis 2 and therefore encompassed less data variance as vectors corresponding with axis 1. In addition, pH and clay content vectors also grouped with distance and plant cover, and the TDN vector ran somewhat parallel with the Al^{3+} vector.

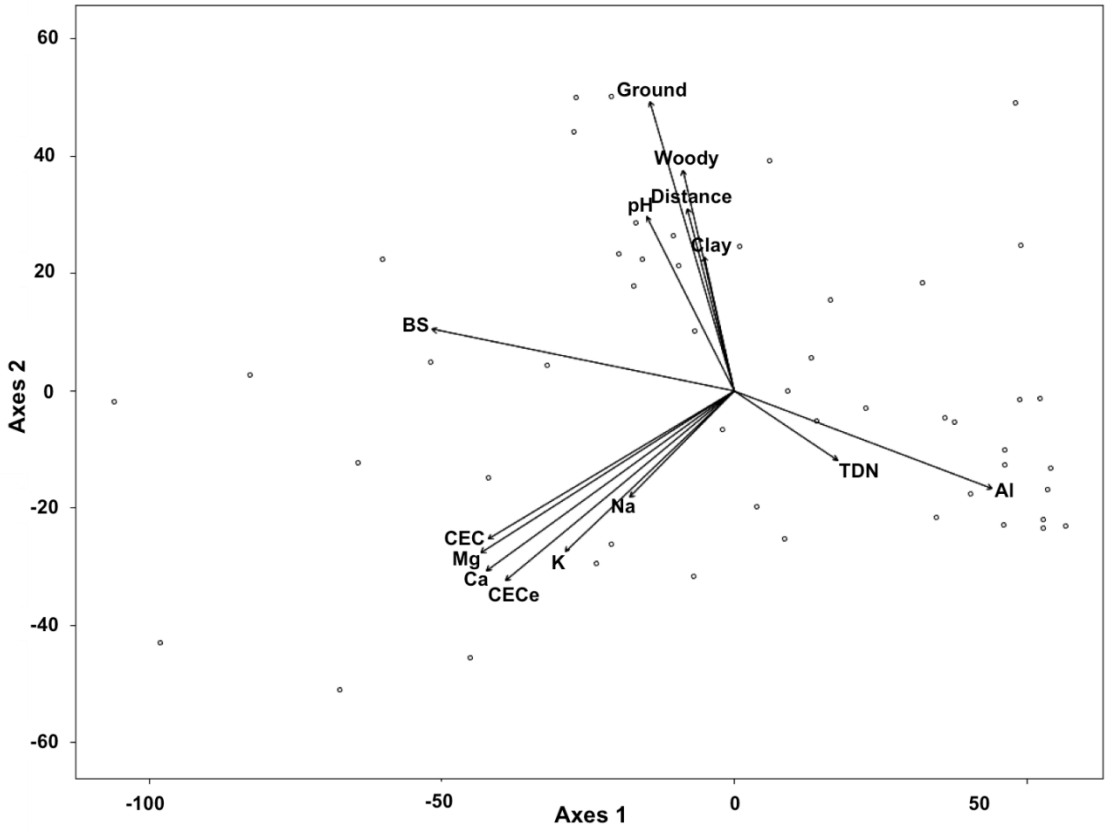

Fig. 4.9. Ordination displaying north and south transect points that had mineral sub-surface (5- to 15-cm) samples, and significant ($P \leq 0.05$) vectors of variables analyzed in those samples. Note: Ground = percentage ground species cover, Woody = percentage woody species cover, Distance = distance from the smelting stack, pH = soil pH, Clay = percentage clay content, BS = percent base saturation, Al = aluminum, TDN = total dissolved nitrogen, Na = sodium, K = potassium, CEC = total cation exchange capacity, Mg = magnesium, Ca = calcium and CECe = effective cation exchange capacity.

Although %BS and Al^{3+} had the greatest correlation to the ordination and corresponded to axis 1 (which encompasses the majority of variance explained by the ordination), the Al^{3+} vector ran roughly perpendicular to cation and cation exchange

vectors, as well as to distance and plant cover vectors. Among cation and cation exchange vectors, Ca^{2+}, Mg^{2+} and CECe had the highest correlations to the ordination (Table 4.5). The distance and percentage plant cover vectors had a higher correlation to the ordination in comparison to pH and %clay vectors, which ran parallel with the distance and plant, cover vectors.

Based on the direction of gradients of vectors in relation to plotted points in Fig. 4.9, some trends with regards to distance and plant cover, can be extrapolated from the sub-surface mineral sample ordination. Similar to the surface sample trends, points within close proximity to the smelter have low percentage ground and woody cover as well as low pH. However, the same vector trends between %clay with distance, ground species cover and woody species cover may also be attributed to contrasting relationships with other variables (discussed above), as Spearman's rho correlations (Tables A.6 to A.13 in Appendix A) also identified no significant ($P \leq 0.05$) relationship between %clay in mineral sub-surface samples with distance, ground species cover or woody species cover.

Organic Samples

The ordination for north and south transect organic surface (0- to 5-cm) samples (Fig. 4.10) utilized a three axes model, however the ordination projection was created with axes 1 and 2 only. The three-axes ordination solution converged after four tries and resulted in a stress of 4.6%. The Shepard diagram identified a non-metric fit r^2 of 0.995 and a linear fit r^2 of 0.974, indicating a good fit of dataset to the ordination. Vectors representing all variables that had a significance of $P \leq 0.05$ are plotted; r^2 and P values of all variable vectors (for axes 1 and 2 but based on the three axes model) are displayed in Table 4.5. The vectors most highly correlated to the organic surface sample ordination were Ca^{2+}, CECe and Mg^{2+} and vectors generally grouped into two themes: 1) cation and cation exchange (including %BS and Al^{3+}); and 2) soil and SOM nutrient quantity. In addition, percentage ground cover and percentage woody cover also grouped with the SOM quantity vectors; however the woody cover vector ran in the opposite direction of the SOM, and percentage ground cover vectors. Furthermore, the cation and cation exchange vectors grouped closer with %BS in comparison to the mineral sample ordination diagrams, and distance from the smelter and pH were not significantly ($P \leq 0.05$) correlated with this ordination.

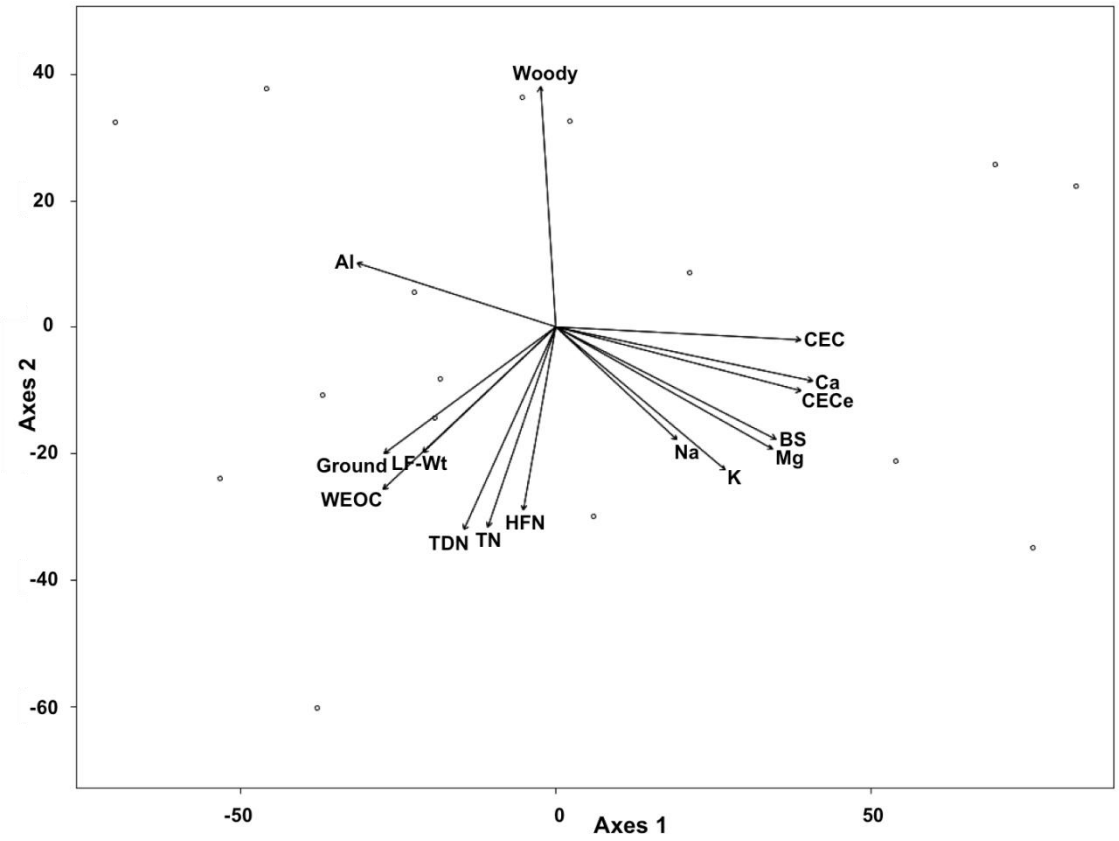

Fig. 4.10. Ordination displaying north and south transect points that had organic surface (0- to 5-cm) samples, and significant ($P \leq 0.05$) vectors of variables analyzed in those samples. Note: Al = exchangeable aluminum, Woody = percentage woody species cover, CEC = total cation exchange capacity, Ca = exchangeable calcium, CECe = effective cation exchange capacity, BS = percent base saturation, Mg = exchangeable magnesium, K = exchangeable potassium, Na = exchangeable sodium, HFN = heavy fraction nitrogen, TN = whole soil total nitrogen, TDN = total dissolved nitrogen, LF-Wt = light fraction weight as a percentage of sample mass, WEOC = water extractable organic carbon, Ground = percentage ground species cover.

Among the cation and cation exchange vectors, Ca^{2+}, CECe and Mg^{2+} were most highly correlated to the ordination (Table 4.5) and all cation and cation exchange vectors grouped closer with %BS, in contrast to the mineral sample ordinations. Similar to the mineral ordination diagrams, however, the cation and cation exchange vectors, as well as the %BS vector, ran opposite to the Al^{3+} vector. Although these vectors were highly correlated to the ordination, they ran roughly perpendicular to ground cover and woody cover, indicating that plant cover is more related with soil and SOM nutrient quantity variables.

Among the soil and SOM nutrient quantity vectors, WEOC, TDN and soil TN were most highly correlated to the ordination (Table 4.5); however percentage woody cover was more strongly correlated to the ordination than SOM and ground cover vectors. The WEOC and LF-Wt vectors were more closely grouped to the ground cover vector, and TDN, TN and HF-N ran roughly opposite the woody cover vector.

Based on the direction of gradients of vectors in relation to plotted points in Fig. 4.10, some trends relating to plant cover were extrapolated from the ordination diagram. Points with higher soil and SOM nutrient content have higher percentage ground cover (and vice versa), but lower woody cover. The relationship directions between the variables in the ordination with ground and woody cover are somewhat supported by Spearman's rho correlations (Tables A.6 to A.13 in Appendix A); however the vectors in the ordination identify more significant variables in comparison to results from Spearman's rho correlations.

The ordination for north and south transect organic sub-surface (5- to 15-cm) samples (Fig. 4.11) utilized a two axes model, and the solution converged after three tries, resulting in a stress of 7.1%. The Shepard diagram identified a non-metric fit r^2 of 0.995 and a linear fit r^2 of 0.975, indicating a good fit of dataset to the ordination. Vectors representing all variables that had a significance of $P \leq 0.05$ are plotted; r^2 and P values of all variable vectors (for axes one and two but based on the three axes model) are displayed in Table 4.5. The vectors most highly correlated to the organic sub-surface sample ordination were woody cover, %BS and total CEC and vectors grouped into one group – cation and cation exchange (including %BS and Al^{3+}). Percentage ground cover and percentage woody cover vectors ran roughly perpendicular to the cation and cation exchange group of vectors; however the ground and woody cover vectors did not run close to one another. Based on these results, few trends can be extrapolated from the diagram with regards to relationships between soil variables with ground species cover and woody species cover. Further exploration of relationships between distance, ground cover and woody cover with the soil variables did not identify any significant ($P \leq 0.05$) relationships (Tables A.6 to A.13 in Appendix A).

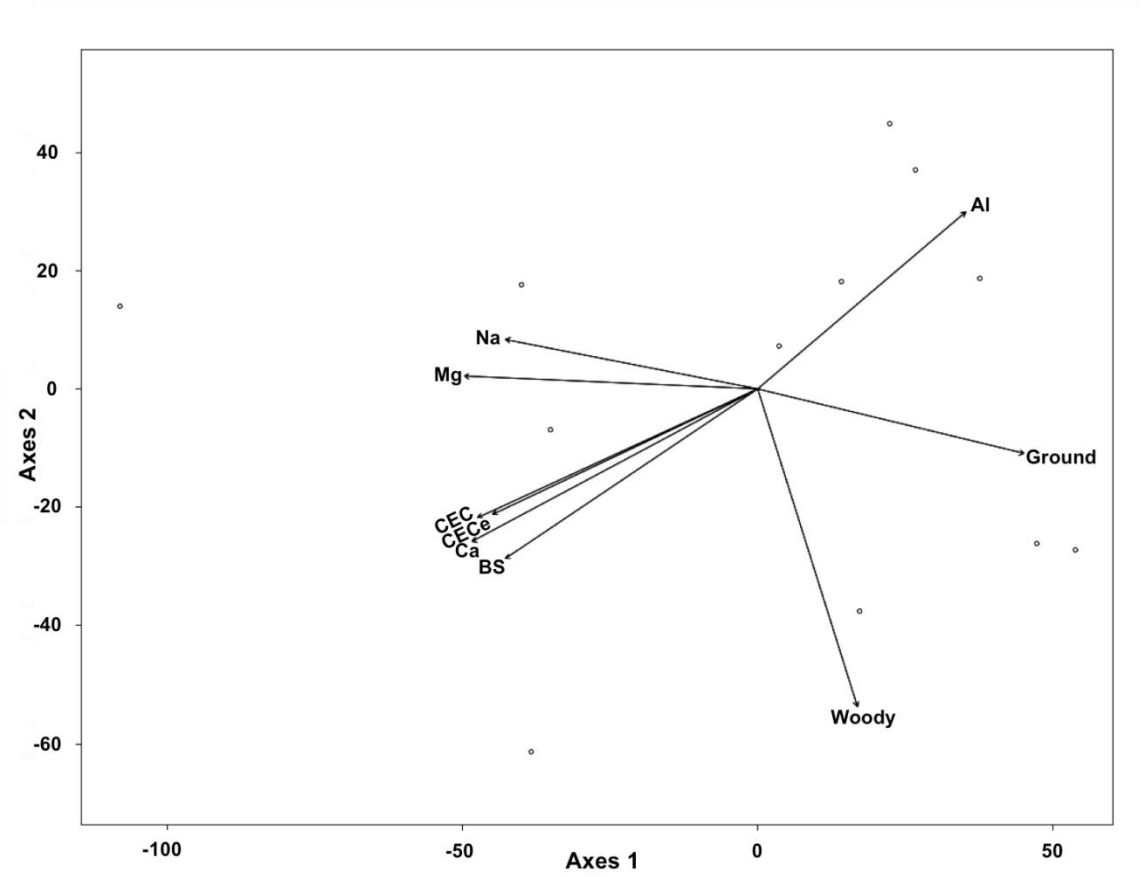

Fig. 4.11. Ordination displaying north and south transect points that had organic sub-surface (5- to 15-cm) samples, and significant (P ≤ 0.05) vectors of variables analyzed in those samples. Note: Mg = exchangeable magnesium, Na = exchangeable sodium, Al = exchangeable aluminum, Ground = percentage ground species cover, Woody = percentage woody species cover, CEC = total cation exchange capacity, CECe = effective cation exchange capacity, Ca = exchangeable calcium and BS = percent base saturation.

4.3 Evaluation of Variables Based on Direction Around the Smelter Stack

4.3.1 Soil classification and percentage plant cover

The parent material and range of texture classes of soils at grid points was the same as those identified at transect sample points (Sect. 4.1.1). Soil orders identified at grids points also were the same as those found at transect point locations; a summary of soil classification results is displayed in Table A.1 in Appendix A. Several points also exhibited a peaty phase upper horizon, therefore, soil samples from the grids also were grouped as mineral (<17% TOC) or organic (> 17% TOC) soils (Soil Classification Working Group, 1998). The pH of mineral and organic samples was also similar to pH values of transect soil samples; however, due to the variability in the number of mineral

and organic samples from each grid the pH values of grids were statistically different ($P \leq 0.05$). The median, minimum and maximum of percentage ground species and woody species cover are displayed in Table 4.6. Plant species identified at grid sample points were similar to those identified at transect sample points (Sect. 4.1.1) and ground species and woody species cover were statistically similar for all grids ($P \leq 0.05$).

Table 4.6. Median (Med), minimum (Min) and maximum (Max) of percentage ground species and woody species cover for eight grids established at each of the major cardinal and ordinal directions around the smelting stack (nine sampling points per grid).

Grid	Ground Species Cover			Woody Species Cover		
	Med	Min	Max	Med	Min	Max
	----- % -----					
North	20	1	90	20	0	70
Northeast	80	1	100	20	1	80
East	1	< 1‡	60	10	1	70
Southeast	50	20	100	20	10	50
South	60	0	100	< 1	0	70
Southwest	25	< 1	100	10	0	20
West	10	1	100	1	0	60
Northwest	50	< 1	100	20	< 1	60

‡ Percentage plant cover <1 indicates area is nearly void of vegetation, but not so much as to be classified as barren (0% cover).

4.3.2 Directional effects

The number of mineral and organic samples varied among grids (Table 4.7). The east and south grids each had the highest proportion of mineral samples (eight out of nine samples) and the northwest grid had the highest proportion of organic samples (eight out of nine samples). After standardization for TOC (due to the variation in the number of mineral and organic samples) total CEC, %BS, Al^{3+}, Ca^{2+}, Mg^{2+}, C:N and TS were significantly ($P \leq 0.05$) different across grids. The median, minimum and maximum of those variables for each grid (based on combined results of all nine samples for each grid) are listed in Table 4.7. The highest total CEC, Ca^{2+} and Mg^{2+} were found in samples from the west, southeast and north grids, respectively; the northeast grid had the lowest values for total CEC, Ca^{2+} as well as Mg^{2+}. The west grid had the highest Al^{3+} content and conversely the lowest %BS; the north, southeast and northwest grids all had the lowest Al^{3+} content (0 $cmol_{(c)}$ kg^{-1} soil) and also the highest %BS (100%). The southeast grid had the highest TS content of all the grids and the east grid had the lowest TS content.

The northwest grid had both the highest soil C:N and soil pH; however, the southeast grid had the lowest soil C:N and the west grid had the lowest soil pH.

Table 4.7. Median, minimum and maximum of values for variables that are significantly different ($P \leq 0.05$) among eight grids established at each of the major cardinal and ordinal directions around the smelting stack. The number of mineral (Min) and organic (Org) soil samples removed from each grid (n = 9 per grid) are also listed.

Grid	n		CEC	Ca^{2+}	Mg^{2+}	Al^{3+}	BS	TS	C:N	pH
	Min	Org	----- $cmol_{(c)}$ kg^{-1} soil -----				--- % ---			
North	7	2								
Med			8.69	44.64	9.94	0.00	100	0.07	23.87	4.59
Min			2.36	0.28	0.13	0.00	5.77	0.01	16.73	4.33
Max			33.29	84.32	11.90	8.78	100	0.29	29.23	5.64
Northeast	3	6								
Med			7.67	1.07	0.12	1.75	75.28	0.37	22.82	5.56
Min			3.13	0.24	0.03	0.00	5.13	0.01	15.91	4.23
Max			55.59	51.78	10.44	8.72	100	0.88	26.52	6.74
East	8	1								
Med			34.58	1.96	0.39	0.85	81.89	0.01	21.05	4.77
Min			5.68	0.49	0.11	0.00	9.25	0.01	17.56	3.90
Max			59.91	18.07	4.56	7.82	100	0.16	44.38	5.53
Southeast	2	7								
Med			9.32	59.73	5.53	0.00	100	0.41	19.29	5.59
Min			4.16	2.16	0.51	0.00	61.07	0.01	17.82	5.08
Max			43.40	75.29	20.89	2.17	100	0.64	24.38	6.86
South	8	1								
Med			28.88	1.91	0.48	2.22	49.42	0.08	22.32	4.73
Min			6.74	0.43	0.06	0.00	10.44	0.01	15.89	4.04
Max			39.60	68.42	8.07	8.60	100	0.27	26.25	5.78
Southwest	5	4								
Med			13.74	2.02	1.78	2.96	89.12	0.08	22.35	4.40
Min			6.75	0.45	0.08	0.00	7.24	0.01	17.41	3.82
Max			44.66	76.09	6.71	8.45	100	0.47	32.15	5.72
West	5	4								
Med			37.26	2.29	0.22	5.08	28.87	0.07	22.72	4.30
Min			8.19	0.30	0.10	0.00	5.65	0.02	19.20	3.97
Max			71.00	39.49	5.50	13.95	100	0.31	28.10	5.28
Northwest	1	8								
Med			23.40	55.10	6.26	0.00	100	0.31	27.96	5.87
Min			7.06	0.22	0.03	0.00	7.40	0.03	17.53	3.89
Max			56.54	70.38	13.40	4.65	100	0.58	44.44	6.18

5. DISCUSSION

Although plant cover in mineral soils increased with distance from the smelter (Figs. 4.8 and 4.9), this does not necessarily identify the smelter (or emissions from the smelter) as the sole contributor to reduced plant cover. Distance was not a significant ($P \leq 0.05$) vector on either organic ordination (Figs. 4.10 and 4.11) but percentage ground and woody cover vectors were significant for both the 0- to 5-cm and 5- to 15-cm organic sample depth ordinations. Therefore, given the greater significance of plant cover in comparison to distance from the smelter, relationships between plant cover and SOM, nutrient and other soil variables should give more insight into the factors contributing to inconsistent revegetation in the area, in comparison to spatial proximity to the smelter. This is similar to the findings by Ginocchio (2000), who found soil N and OM content were more important than smelter-derived Cu and S in soil when identifying variation in plant species abundance around a smelter in central Chile. Percentage ground species and woody species cover ranged from dense boreal forest cover (100%), to barren with no cover (0%), similar to what has been identified in other smelter-affected areas (Gignac and Beckett, 1986; Brais et al., 1995; Ginocchio, 2000; Salemaa et al., 2001; Kiikkila, 2003; Kozlov and Zvereva, 2007; Anderson et al., 2009). However, some of the variability in ground and woody species cover and soil analyses results can be attributed to soil parent material (i.e., organic or mineral; sand vs. clay) and landscape position (among steep rock outcrops), in addition to natural or anthropogenic disturbances. The majority of findings from this study are consistent with those found in previous studies (Table 5.1).

5.1 Soil organic matter fraction characteristics

Water extractable organic carbon is a highly mobile and labile SOM fraction that is readily available to microorganisms and plants and, therefore, is critical to the productivity of forest environments. The WEOC values in both mineral and organic samples in this study were far (approximately two orders of magnitude) below what has been found in other impacted and non-impacted forest soils (Boyer and Groffman, 1996; Zsolnay, 1996; Seguin et al., 2004; Ostrowska et al., 2010) and were coupled with low

Table 5.1. Summary of results from relevant literature of select soil organic matter, soil nutrient and cation exchange variables analyzed in this study, as well as the median results from this study of those variables. Results reported from this study are the median data for mineral samples and organic samples for the north transect and south transect separately. In the columns, north transect data are reported followed by south transect data (i.e., north transect, south transect).

Characteristic	Results	Study Location	Reference	Results: This Study	
				Mineral	Organic
LF-Wt, %	6.4 – 11.1	Coniferous forests – USA	Sollins et al. (1984)	0.43, 1.23	31.99, 18.75
	3.6	Coniferous forest – USA	Crow et al. (2007)		
	3.8 – 10.4	Spruce forest – Austria	Schindlbacher et al. (2010)		
LF-C, %	10.2 – 32.7	Coniferous forests – USA	Sollins et al. (1984)	36.30, 37.70	41.75, 44.30
	28.7	Coniferous forest – USA	Crow et al. (2007)		
LF-N, %	0.20 – 0.87	Coniferous forests – USA	Sollins et al. (1984)	0.77, 1.15	1.37, 1.43
	0.5	Coniferous forest – USA	Crow et al. (2007)		
LF-C:N	38.6 – 55.4	Coniferous forests – USA	Sollins et al. (1984)	45.83, 31.64	28.51, 27.93
	18.2	Forest soils - Review	Gregorich et al. (2006)		
	30	Spruce forest - Germany	Spielvogel et al. (2006)		
	21	Spruce forest - Germany	Spielvogel et al. (2006)		
	60.7	Coniferous forest – USA	Crow et al. (2007)		
	40 - 60	Boreal forest - Canada	Norris et al. (2011)		
HF-C, %	1.2 – 10.4	Coniferous forests – USA	Sollins et al. (1984)	2.60, 3.40	26.90, 19.20
	4.9	Coniferous forest – USA	Crow et al. (2007)		
HF-N, %	0.052 – 0.446	Coniferous forests – USA	Sollins et al. (1984)	0.13 – 0.86	0.91 – 1.32
	0.2	Coniferous forest – USA	Crow et al. (2007)		
HF-C:N	22.1 – 23.6	Coniferous forests – USA	Sollins et al. (1984)	32.03, 18.32	21.45, 18.32
	29.9	Coniferous forest – USA	Crow et al. (2007)		
WEOC, mg C kg^{-1} soil	0.2 – 949	Deciduous forest – USA	Boyer and Groffman (1996)	2.22, 3.08	27.10, 38.97
	~ 10 – 650 (mineral)	Forest soils – review paper	Zsolnay (1996) (and sources within)		
	~ 1000 – 2400 (organic)	Forest soils – review paper	Zsolna, (1996) (and sources within)		
	370 – 920	Trembling aspen forest – Canada	Seguin et al. (2004)		
	370 – 610	Mixed forest - Canada	Seguin et al. (2004)		
	28 – 164	Pine forest – Poland	Ostrowska et al. (2010)		
	3410	Pine forest - Poland	Ostrowska et al. (2010)		

Table 5.1 (continued). Summary of results from relevant literature of select soil organic matter, soil nutrient and cation exchange variables analyzed in this study, as well as the median results from this study of those variables. Results reported from this study are the median data for mineral samples and organic samples for the north transect and south transect separately. In the columns, north transect data are reported followed by south transect data (i.e., north transect, south transect).

Characteristic	Results	Study Location	Reference	Results: This Study	
				Mineral	Organic
Soil C:N	11.5 – 13.5 (mineral)	Forest soils – review paper	Batjes (1996)	26.57, 18.55	21.50, 18.55
	25.8 (organic)	Forest soils – review paper	Batjes (1996)		
	21.5 – 24.4	Mixed, clear-cut forest – Canada	Pennock and van Kessel (1997)		
	~ 10 – 30	Temperate forests – review paper	Booth et al. (2005)		
	22	Coniferous forest – USA	Ping et al. (2010)		
	13 – 30	Peatlands - Turkey	Cayci et al. (2011)		
TOC, %	2.0 (mineral)	Coniferous forests - Canada	Meyer et al. (1994)	2.97, 3.22	41.31, 33.70
	0.59 – 1.37 (mineral)	Forest – Brazil (smelter-affected)	Klumpp et al. (2003)		
	18.0 – 36.3	Peatlands - Turkey	Cayci et al. (2011)		
TN, %	0.1 – 1	Temperate forests – review paper	Booth et al. (2005)	0.14, 0.20	1.88, 1.51
	0.78 – 1.82	Peatlands - Turkey	Cayci et al. (2011)		
TS, %	0.43 – 1.15	Peatlands - Turkey	Cayci et al. (2011)	0.02, 0.07	0.32, 0.48
Total CEC, $cmol_{(c)}\ kg^{-1}$ soil	100 – 141	Peatlands - Turkey	Cayci et al. (2011)	10.36, 1.71	8.76, 9.41
	~ 16 – 24 (surface soil)	Background pine forest – Russia	Lukina and Nikonov (2001)		
	~ 5 – 12 (surface soil)	Smelter-affect pine forest – Russia	Lukina and Nikonov, 2001		
	7.7 – 33.1	Smelter-affected grassland – USA	Anderson et al., 2009		
	11.2 – 14.3	Mixed, clear-cut forest – Canada	Pennock and van Kessel (1997)		
	6.0 (mineral)	Coniferous forests – Canada	Meyer et al. (1994)		

Table 5.1 (continued). Summary of results from relevant literature of select soil organic matter, soil nutrient and cation exchange variables analyzed in this study, as well as the median results from this study of those variables. Results reported from this study are the median data for mineral samples and organic samples for the north transect and south transect separately. In the columns, north transect data are reported followed by south transect data (i.e., north transect, south transect).

Characteristic	Results	Study Location	Reference	Results: This Study	
				Mineral	Organic
CECe, $cmol_{(c)}\ kg^{-1}$ soil	72.5 (maximum)	Boreal forest – Canada	Brais et al. (1995)	5.04, 7.04	8.91, 9.98
	111 – 170 (organic layer)	Pine forest – Finland, smelter-affected	Derome and Lindroos (1998)		
	17 – 22 (upper mineral)	Pine forest – Finland, smelter-affected	Derome and Lindroos (1998)		
Base saturation, %	16.8 – 44.1 (organic layer)	Pine forest – Finland, smelter-affected	Derome and Lindroos (1998)	89.76, 37.43	89.63, 55.57
	7.0 – 14.3 (upper mineral)	Pine forest – Finland, smelter-affected	Derome and Lindroos (1998)		
Ca^{2+}, $cmol_{(c)}\ kg^{-1}$ soil	57.6 (maximum)	Boreal forest – Canada	Brais et al. (1995)	2.73, 1.21	5.38, 3.53
Mg^{2+}, $cmol_{(c)}\ kg^{-1}$ soil	11.9 (maximum)	Boreal forest – Canada	Brais et al. (1995)	0.39, 0.51	0.76, 1.02

TDN values (Figs. 4.6 and 4.7). These lower values reflect the sensitivity of WEOC in response to changes in land use and management practices (Chantigny, 2003), which in Flin Flon-Creighton includes historical clear-cutting, deforestation and forest dieback. The loss and/or reduction of forest vegetation cover and associated reduction in root biomass would further contribute to lower WEOC values, as roots contribute high amounts of WEOC to rhizosphere soil (Grayston et al., 1997; Seguin et al., 2004). In addition, low WEOC and TDN content may reflect metal and contaminant complexation with OM in solution (Herbert and Bertsch, 1995), similar to results found in a smelter-affected environment in Quebec, where stronger correlations existed between WEOC and extractable metals (the strongest being Mg and Al) than between extractable metals and the pH of the extract (Seguin et al., 2004). Therefore, within the Flin Flon-Creighton soil environment where smelter-derived metal accumulation has been identified (Franzin et al., 1979; Henderson et al., 1998; McMartin et al., 1999), WEOC may be a significant variable regarding metal-OM complexation and metal availability.

Low WEOC and TDN content reflect hydrology issues that have been evident in other smelter-affected areas, such as drought conditions and lower water table (Gignac and Beckett, 1986), or increased downward water flux beyond what was found under normal forest soil conditions (Derome and Nieminen, 1998). In this study, low WEOC and TDN content, the significance of TDN in sub-surface mineral sample ordination (Fig. 4.9), and statistically similar ($P \leq 0.05$) WEOC and TDN content in surface and sub-surface samples identify reduced transportation and accumulation of SOM in solution. Such issues have negative implications for nutrient transport and availability to vegetation, as WEOC has been identified as a main source of SOM at depth in mineral boreal forest soils (Norris et al., 2011). The low values of WEOC and TDN are likely the result of compounded effects from land use changes, complexation with metals and hydrological changes, all of which contribute to the variability and reduction in plant cover in Flin Flon-Creighton.

The LF and HF characteristics of Flin Flon-Creighton soils were generally within a range similar to those described in other coniferous forest studies, although the LF-Wt of north transect mineral samples was lower than what has been reported (Crow et al., 2007; Schindlbacher et al., 2010; Norris et al., 2011). The wider LF-C:N with increasing

plant cover and increasing distance from the smelter is likely attributed to greater amounts of recent plant biomass inputs, which have wider C:N than more decomposed OM (Gregorich et al., 2006). Conversely, a narrower LF-C:N and higher LF-N and TDN content within areas with low (or no) plant cover–and closer to the smelter–reflect more recalcitrant SOM that has undergone significant decomposition without recent biomass inputs. Similar LF-C:N trends were found in other studies examining forest dieback (Viventsova et al., 2005; Spielvogel et al., 2006), indicating dieback contributes to reduced labile SOM compound concentrations and advanced OM decomposition. The stronger correlation of LF-C:N, in comparison to HF-C:N, to the mineral surface soil ordination (Table 4.5) also reflects the importance of the decomposition state of SOM in mineral soil and that more recent SOM inputs (LF), in comparison to more recalcitrant SOM (HF), better explains plant cover and soil analyses variance. However, because HF has been identified as a source of mineralizable N (although not necessarily controlled by the C:N), and undergoes enhanced mineralization in disturbed soils (Whalen et al., 2000) and LF-N has been correlated with N mineralization (Sollins et al., 1984), more in-depth exploration of mineralization rates in these fractions would give better insight into specific nutrient cycling dynamics in the Flin Flon-Creighton area.

The median LF-Wt in mineral soils was statistically similar for transects, but the south transect had a wider distribution of values due to a greater frequency of high LF-Wt values (Fig. 4.3). The greater accumulation of LF SOM along the south transect could explain why LF-N content was the same for both the mineral and organic samples along the south transect and why there was higher LF-N than in the north transect mineral samples (Fig. 4.6). There was, however, no significant difference ($P \leq 0.05$) in LF-C along the north and south transects and considering this in relation to LF-N, explains the narrower LF-C:N in south transect mineral samples compared to mineral north transect samples (Sect. 4.1.2). This N deficit, and therefore reduced soil quality, in the north transect area indentifies one possible explanation as to why liming treatment by *The Green Project* has been more successful in sites south of the smelter versus north (Price, 2009), as nutrient deficiency may not have been as large an issue in the south transect area.

Although there was higher TDN and LF-N content in soils within close proximity to the smelter, this can also be attributed to more recalcitrant SOM and/or altered SOM decomposition. This is hypothesized based on the alteration of SOM chemical composition in disturbed environments, the more recalcitrant state of SOM after prolonged decomposition (discussed above), and the inability of total N measurement to identify state of lability of SOM compounds (Attiwill and Adams, 1993). As well, similar trends in the vector direction of LF-N and TDN suggests both fractions derive their nutrient status from the same substrate. This would have implications on turnover of OM in solution in Flin Flon-Creighton, as labile (low weight) OM compounds in solution have high mineralization rates and contribute to a high proportion of the OM mineralized in boreal forest soils (van Hees et al., 2005). Furthermore, metal-SOM interactions, especially in the water-extractable fraction may make those fractions unavailable to microorganisms or plants (discussed above). Therefore, although more N may be present in the fractions analyzed in areas with low plant cover and close to the smelter, the SOM compounds containing the N present may not be in forms readily decomposed or available to plants and microorganisms. Further investigation of this hypothesis is required.

In the organic surface sample ordination, grouping of SOM fractions with ground cover (and perpendicular to woody cover) (Fig. 4.10) are likely a consequence of the plant species common in organic soil areas (i.e., mosses, sedges, etc.) as well as the organic parent material that is diagnostic for the organic soil classification (Moore et al., 2007). These relationships are further supported by tight group of N content vectors (TDN, TN, HF-N) and C content vectors (WEOC, LF-Wt which strongly reflects C content). Woody and grounding species cover vectors, however, did not group closely together in surface or sub-surface ordinations, also likely due to the plant species supported by organic soils (i.e., more ground cover species than woody cover species).

5.2 Soil Carbon, Nitrogen and Sulphur

Unlike the trend seen with SOM variable vectors, few soil nutrient vectors were significantly correlated with the mineral or organic sample ordinations (surface and sub-surface). This identifies a more significant influence of SOM fraction quantity and

quality, in comparison to whole soil nutrient status, on the overall variability in the data. Of the whole soil nutrient status indices analyzed, only the TS vector was significantly correlated with the mineral surface sample ordination and had a similar direction gradient as (i.e., increased with) distance, ground cover and woody cover. However, the TS r^2 for the ordination was 0.1213 (Table 4.5), and upon inspection of Spearman's rho correlations it was identified that although there was an inverse relationship between TS and distance as well as woody cover, there were positive correlations between TS and most of the SOM fraction variables (excluding LF- and HF- C:N). This indicates SOM quantity may be a more important factor in TS accumulation in soil, versus distance or woody cover. Furthermore, there was a higher accumulation of TS on surface mineral samples of the south transect in comparison to the north transect (Table 4.2). These trends combined likely reflect higher aerial deposition south of the smelter, possibly due to prevailing wind directions (Franzin et al., 1979) and/or higher accumulation of TS in SOM fractions (Koptsik and Alewell, 2007), which had greater values along the south transect (discussed above). This is supported by higher TS content in organic (median 0.30 to 0.50 %) versus mineral (0.02 to 0.07%) soils (Table 4.2). In organic sample ordinations, only TN was significantly correlated with the surface sample ordination and was closely grouped with TDN and HF-N, owing to the organic nature of the parent material (SOM substrate).

Soil nutrient parameters had similar trends to SOM when comparing data between sample classification, depth and each transect separately. Nutrient content was higher in organic versus mineral soils, with high variability in distribution (Table 4.2). The greater frequency of high LF-Wt and LF-N in south transect mineral surface samples likely explains why TOC and TN distribution varied between mineral sample depth; conversely uniformity in LF results explain why this pattern was not present in north transect mineral surface and sub-surface samples. The difference in distribution of TOC in organic surface and sub-surface samples within the south transect may be attributed to variation in decomposition state of OM organic soils (more decomposed SOM at depth resulting in higher TOC content in sub-surface samples) (Cayci et al., 2011) or due to the presence of several peaty-phase soils, where upper horizons were dominated by organic material and lower horizons were of mineral origin (most likely explanation). Regardless of variations

in TOC and TN content in mineral and organic soils, the C:N of mineral compared to organic soils (~ 20) were not statistically different ($P \leq 0.05$) within either transect, nor were there differences in the C:N between surface and sub-surface samples. This indicates potential accumulation of recalcitrant biomass leading to high soil C and limitation of N in mineral soils, similar to trends identified in SOM analyses. The median whole soil C:N of mineral and organic samples were however within the range identified by reviews of forest soils (Batjes, 1996; Booth et al., 2005), although some mineral samples (especially the from the north transect) had very high (i.e., maximum) C:N ratios (Table 4.2). When comparing between transects, south transect surface mineral samples had higher maximum TN values and lower maximum C:N results which, as mentioned, may indicate an N deficit in north transect mineral soils.

5.3 Cations and Cation Exchange Capacity

In all ordinations cation and cation exchange variables encompassed the majority of dataset variance (vectors ran roughly parallel with axis 1), but respective vectors ran perpendicular to distance, plant cover and SOM vectors indicating that cations and cation exchange are not be directly linked to distance or plant cover (nor SOM quantity and quality). In addition, individual exchangeable cation contents, total CEC, CECe and %BS were the same between mineral and organic classifications (Tables 4.3 and 4.4) indicating that SOM content may not be the dominant controlling factor on cation and cation exchange in the Flin Flon-Creighton area.

Percent BS and Al^{3+} vectors were most strongly correlated to surface mineral sample ordination (Fig. 4.8), reflecting the wide variability of %BS (and related base cation content) and Al^{3+} content of those samples (Tables 4.3 and 4.4). The significance of %BS and base cation content to data variation was also seen in sub-surface mineral samples, where %BS, Ca^{2+} and Mg^{2+} vectors were mostly strongly correlated to the ordination (Fig. 4.9). The high significance of Ca^{2+} and Mg^{2+} vectors in the sub-surface mineral ordination (Fig. 4.8) may identify migration and accumulation of Ca^{2+} and Mg^{2+} ions in the sub-surface (Derome and Nieminen, 1998).

Furthermore, the median %BS was higher in north transect versus south transect mineral samples (and higher Al^{3+} in both depths of mineral samples along the south

transect versus the north) (Table 4.3). The between-transect differences may be related to historical fire disturbances in the area, or the influence of soil acidity and Al^{3+} availability, both of which can affect CEC (Ross et al., 2008) and may further indicate why dolomite limestone application has been more successful at revegetating sites south of the smelter compared to the already base-rich area north of the smelter (Price, 2009).

Soil pH, clay content and SOM content have been identified as the main influences on CEC and cation content in forest soils (Meyer et al., 1994; Ross et al., 2008). In addition, inverse relationships have been identified between CEC, Ca^{2+}, Mg^{2+} and K^{+} and Al^{3+} concentrations in soil and distance from a smelter, as well as positive relationships between those variables and SOM and plant cover in that smelter-affected environment (Lukina and Nikonov, 2001). However, in this study cation and cation exchange vector did not group with pH, clay or SOM vectors in the ordinations, nor with distance from the smelter, suggesting that other disturbances in addition to the smelter may be affecting cation and cation exchange in the Flin Flon-Creighton soil environment.

5.4 Disturbance Effects

Clear cutting can lead to the eventual reduction of CEC and cation content. In a northern Saskatchewan mixed-wood forest the %BS and CEC increased up to five years after clear cutting, but from six to 20 years after clear cutting declined to below levels of a mature forest (Pennock and vanKessel, 1997). As well, a review of relevant literature and analysis of datasets identified relatively little affect of tree harvesting on soil C and N. However, removal of residue from the soil surface can have a negative affect on C and N content in upper mineral soil horizons (Johnson and Curtis, 2001). Furthermore, those trends also indicated that prescribed burning after tree harvest can reduce soil C content.

In contrast, forest fire has been identified as a mechanism for ‘initially” increasing soil cation content and cation exchange, although not “permanently”. Forest fire specifically increases exchangeable Ca^{2+} and Mg^{2+} and %BS due to combustion of SOM, but decreases CEC based on the amount of OM lost from the soil environment (Certini, 2005). Along a post-fire succession gradient, Brais et al. (1995) identified the highest soil CECe, Ca^{2+}, Mg^{2+} and K^{+} content approximately 50 years after forest fire, which declined with time (although spikes in CECe and Ca^{2+}, were identified between 150 and

200 years after fire). Therefore, based on this, forest fires can have long-term positive affects on the quality (exchangeable cation content) of forest soils, aiding in forest vegetation succession. In addition, forest fires have been shown to alter soil C and N and SOM. Some studies have identified that the impact of fire on SOM is dependent on the length and intensity of the forest fire, however fires generally cause increased inorganic N content, long-term immobilization of organic N, and formation of recalcitrant SOM (including WEOM) structures (Certini, 2005; Knicker, 2007; Thiffault et al., 2008; Vergnoux et al., 2011). In addition, in organic soils comprised of *Sphagnum* species, forest fire can increase recalcitrant SOM content and hinder decomposition of organic substrate (O'Donnell et al., 2009). Although fresh biomass inputs from forest vegetation are presumed to offset these recalcitrant structures, in areas such as Flin Flon-Creighton where inputs have been reduced or completely hindered, historical forest fires likely have a stronger influence on SOM quantity than in other forest environments.

5.5 Directional Effects

Finally, grid sample analysis was conducted to understand differences based on direction identified total CEC, Ca^{2+}, Mg^{2+}, Al^{3+}, %BS, TS, C:N and pH were different between grids (Table 4.7). The cation and cation exchange variables that differed between grids were also some of the most significant vectors in the ordinations examined (Figs. 4.8 – 4.11). The reasoning behind the significance of the cation and cation exchange variables (discussed above) also explains the variability in results seen within grid samples. Furthermore, differences in TS content of soil samples may indicate differences in aerial deposition from the smelter as the highest TS content was in the southeast grid which was identified as one of the dominant wind directions (Franzin et al., 1979; McMartin et al., 1999). However, the number of organic versus mineral samples also likely influence the differences in TS, as organic substances have been found to have higher TS and organic S content near a smelter, in comparison to mineral soil samples (Koptsik and Alewell, 2007). Lastly, C:N and pH differed based on direction; however, the values for each variable were similar to those identified in transect samples and were within a normal range for soil C:N and pH of boreal forest soils.

6. CONCLUSION

Overall, ground and woody species cover are more related to SOM quality and quantity than other variables, including distance from the smelter. Although cation and cation exchange variables contribute to more of the data variance, they were unrelated to distance and plant cover. Soil organic matter quality and quantity indices provide insight into inconsistent natural and assisted revegetation throughout the Flin Flon, Manitoba and Creighton, Saskatchewan area. Specifically, LF and HF SOM, as well as N content in SOM fractions and in whole soils, are of particular interest when considering inconsistent revegetation and total nutrient status of whole soils are less effective in explaining revegetation inconsistencies. Therefore, it is suggested SOM quality and quantity results be considered when designing revegetation strategies in the Flin Flon-Creighton area.

Recommendations for future studies in the Flin Flon-Creighton area include the analysis and identification of what specific organic compounds and functional groups comprise SOM fractions in the Flin Flon-Creighton soil environment, as it may give further insight into what proportion of the SOM present is in forms readily available to microorganisms and plants. In addition, a suitable technique for microbial biomass measurement that takes into account the presence of charcoal within forest soils would also be beneficial in producing reliable results regarding the size of microbial populations in this environment. Although identifying the direct cause (i.e. anthropogenic or natural disturbance) of plant cover variability is not within the scope of this study, understanding the possible influence of forest fire and deforestation on soils in Flin Flon-Creighton will likely increase the effectiveness of ecorestoration strategies in the area. Lastly, as Zoltai (1988) identified accumulation of smelter-derived metals in organic soils surrounding the Flin Flon smelter, a more in depth examination of organic soil properties (organic compounds, metal availability) in the area and possible relationships with vegetation cover based on spatial proximity to the smelter is recommended.

In conclusion, it is recommended that using the previously discussed SOM quality and quantity indices is beneficial in identifying the general quality of soil conditions throughout the Flin Flon-Creighton area. Specifically, indices that should be focused on when designing revegetation strategies in the area include the quantity of labile organic

matter (such as LF and WEOC) and the N content of labile SOM fractions, as well as OM sources. Furthermore, the analysis of SOM fractions, their C and N content as well as their chemical composition may give insight into dieback and regeneration inhibition in other areas affected by non-ferrous smelting.

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APPENDIX A

Table A.1. Frequency of various soil pit classifications from all sampling locations (transects and grids) in the present Flin Flon-Creighton study. Classification were made according to the Canadian System of Soil Classification(Soil Classification Working Group, 1998).

Soil Classification	North Transect	South Transect	North Grid	Northeast Grid	East Grid	Southeast Grid	South Grid	Southwest Grid	West Grid	Northwest Grid	Total
Eluviated Dystric Brunisol	3	2	2	-	4	-	3	-	-	-	14
Gleyed Eluviated Dystric Brunisol	2	-	-	-	1	-	-	-	-	-	3
Orthic Dystric Brunisol	3	4	1	1	2	1	3	4	6	3	28
Typic Fibrisol	3	2	1	7	-	4	-	2	-	2	21
Rego Gleysol	3	1	-	-	1	-	-	-	1	-	6
Orthic Gray Luvisol	-	-	-	-	-	1	1	1	-	-	3
Cumulic Regosol	-	6	-	-	-	1	-	-	-	-	7
Orthic Regosol	17	16	5	1	1	2	2	2	2	4	52

Table A.2. Mean, standard deviation (SD) (in brackets), median (Med), minimum (Min) and maximum (Max) of variables analyzed in north transect surface (0- to 5-cm) and sub-surface (5- to 15-cm) mineral samples. Dashes indicate the variable was not measured in that sample.

	Surface				Sub-Surface			
	Mean (SD)	Med	Min	Max	Mean (SD)	Med	Min	Max
WEOC (mg C kg^{-1} soil)	2.72 (1.34)	2.22	0.57	5.99	1.94 (1.21)	1.78	0.00	4.66
TDN (mg C kg^{-1} soil)	0.59 (0.41)	0.51	0.2	1.65	0.44 (0.34)	0.36	0.00	1.27
LF-Wt (%)	0.96 (0.91)	0.43	0.10	2.93	-	-	-	-
LF-C (%)	35.45 (5.44)	36.30	22.90	42.50	-	-	-	-
LF-N (%)	0.78 (0.25)	0.77	0.32	1.25	-	-	-	-
LF-C:N	49.97 (18.49)	45.83	32.83	116.30	-	-	-	-
HF-C (%)	3.22 (1.98)	2.60	0.64	9.03	-	-	-	-
HF-N (%)	0.12 (0.11)	0.86	0.03	0.44	-	-	-	-
HF-C:N	33.28 (15.13)	32.03	9.22	59.77	-	-	-	-
TOC (%)	3.33 (2.10)	2.97	0.53	7.97	2.41 (2.02)	1.89	0.24	8.54
TN (%)	0.15 (0.10)	0.14	0.04	0.44	0.14 (0.12)	0.10	0.02	0.54
C:N	27.87 (9.64)	26.57	13.65	51.50	25.36 (15.50)	21.06	5.02	79.50
TS (%)	0.03 (0.04)	0.02	0.01	0.15	0.03 (0.19)	0.02	0.01	0.08
pH	4.56 (0.26)	4.54	4.10	5.11	4.77 (0.40)	4.70	4.27	5.76
CEC ($cmol_{(c)}$ kg^{-1} soil)	14.21 (9.97)	10.36	4.77	38.14	16.8 (16.92)	11.16	2.16	73.90
CECe ($cmol_{(c)}$ kg^{-1} soil)	11.54 (15.56)	5.04	0.83	56.50	14.65 (25.93)	3.75	0.59	82.14
Ca^{2+} ($cmol_{(c)}$ kg^{-1} soil)	8.33 (14.31)	2.73	0.20	50.13	11.59 (23.59)	1.19	0.08	73.56
Mg^{2+} ($cmol_{(c)}$ kg^{-1} soil)	1.25 (1.82)	0.39	0.00	6.25	1.45 (2.62)	0.20	0.00	8.35
Na^{+} ($cmol_{(c)}$ kg^{-1} soil)	0.11 (0.22)	0.07	0.00	1.05	0.11 (0.25)	0.06	0.00	1.27
K^{+} ($cmol_{(c)}$ kg^{-1} soil)	0.28 (0.22)	0.16	0.08	0.83	0.21 (0.18)	0.16	0.00	0.60
Al^{3+} ($cmol_{(c)}$ kg^{-1} soil)	1.57 (2.47)	0.34	0.00	8.60	1.30 (1.86)	0.26	0.00	6.56
%BS	74.11 (33.78)	89.76	8.92	100.00	70.23 (33.96)	82.29	5.76	100.00

Table A.2. Mean, standard deviation (SD) (in brackets), median (Med), minimum (Min) and maximum (Max) of variables analyzed in north transect surface (0- to 5-cm) and sub-surface (5- to 15-cm) mineral samples. Dashes indicate the variable was not measured in that sample (continued).

	Surface				Sub-Surface			
	Mean (SD)	Med	Min	Max	Mean (SD)	Med	Min	Max
%Clay	4.29 (6.55)	0.87	0.00	20.19	5.76 (8.60)	0.90	0.00	34.78

Table A.3. Mean, standard deviation (SD) (in brackets), median (Med), minimum (Min) and maximum (Max) of variables analyzed in north transect surface (0- to 5-cm) and sub-surface (5- to 15-cm) organic samples. Dashes indicate the variable was not measured in that sample.

	Surface				Sub-Surface			
	Mean (SD)	Med	Min	Max	Mean (SD)	Med	Min	Max
WEOC (mg C kg^{-1} soil)	28.17 (16.75)	27.10	3.12	58.85	37.67 (19.45)	37.57	9.09	61.12
TDN (mg N kg^{-1} soil)	4.37 (3.65)	4.44	11.78	11.78	4.02 (3.03)	2.97	1.06	9.26
LF-Wt (%)	32.44 (15.72)	31.99	13.30	58.41	-	-	-	-
LF-C (%)	41.48 (4.96)	41.75	31.10	48.00	-	-	-	-
LF-N (%)	1.42 (0.28)	1.37	1.13	1.87	-	-	-	-
LF-C:N	30.04 (6.40)	28.51	22.14	42.48	-	-	-	-
HF-C (%)	28.46 (5.19)	26.90	22.60	15.40	-	-	-	-
HF-N (%)	1.38 (0.32)	1.32	1.05	1.91	-	-	-	-
HF-C:N	21.26 (4.55)	21.45	16.19	28.87	-	-	-	-
TOC (%)	40.74 (5.48)	41.31	30.66	47.70	43.43 (5.31)	46.56	35.94	47.26
TN (%)	1.86 (0.29)	1.88	1.40	2.25	1.87 (0.40)	1.90	1.38	2.50
C:N	22.31 (5.53)	21.50	17.05	33.86	23.83 (5.49)	23.73	18.32	33.70
TS (%)	0.37 (0.19)	0.32	0.20	0.73	0.49 (0.29)	0.37	0.24	0.91
pH	5.50 (0.23)	5.56	5.11	5.83	5.63 (0.40)	5.53	4.94	6.39
CEC ($cmol_{(c)}$ kg^{-1} soil)	16.49 (14.09)	8.76	6.12	43.67	14.21 (14.32)	9.49	3.17	42.73
CECe ($cmol_{(c)}$ kg^{-1} soil)	19.98 (26.07)	8.91	2.10	77.15	14.66 (18.15)	7.29	5.40	51.60
Ca^{2+} ($cmol_{(c)}$ kg^{-1} soil)	15.28 (22.22)	5.38	0.47	63.27	8.48 (14.73)	2.80	0.38	38.25
Mg^{2+} ($cmol_{(c)}$ kg^{-1} soil)	2.60 (4.06)	0.76	0.00	11.50	2.09 (4.17)	0.42	0.00	10.57
Na^{+} ($cmol_{(c)}$ kg^{-1} soil)	0.11 (0.22)	0.10	0.00	1.70	0.11 (0.25)	0.09	0.00	2.30
K^{+} ($cmol_{(c)}$ kg^{-1} soil)	0.28 (0.22)	0.37	0.15	0.56	0.21 (0.18)	0.15	0.10	0.40
Al^{3+} ($cmol_{(c)}$ kg^{-1} soil)	1.57 (2.47)	0.58	0.00	5.34	1.30 (1.86)	3.67	0.00	6.81
%BS	75.26 (31.59)	89.63	14.32	100.00	54.23 (40.91)	53.60	8.11	100.00

Table A.4. Mean, standard deviation (SD) (in brackets), median (Med), minimum (Min) and maximum (Max) of variables analyzed in south transect surface (0- to 5-cm) and sub-surface (5- to 15-cm) mineral samples. Dashes indicate the variable was not measured in that sample.

	Surface				Sub-Surface			
	Mean (SD)	Med	Min	Max	Mean (SD)	Med	Min	Max
WEOC ($mg\ C\ kg^{-1}$ soil)	4.39 (5.39)	3.08	0.00	26.26	5.69 (9.40)	2.21	0.68	36.27
TDN ($mg\ N\ kg^{-1}$ soil)	1.10 (1.71)	0.51	0.00	7.75	0.77 (1.26)	0.24	0.00	4.60
LF-Wt (%)	4.28 (9.01)	1.23	0.26	43.68	-	-	-	-
LF-C (%)	37.44 (5.75)	37.70	26.60	47.70	-	-	-	-
LF-N (%)	1.24 (0.47)	1.15	.69	2.25	-	-	-	-
LF-C:N	33.18 (9.70)	31.64	16.80	54.32	-	-	-	-
HF-C (%)	4.57 (3.47)	3.40	0.84	13.30	-	-	-	-
HF-N (%)	0.35 (0.63)	0.13	0.01	3.01	-	-	-	-
HF-C:N	27.45 (16.20)	24.46	2.91	77.31	-	-	-	-
TOC (%)	5.52 (4.56)	3.22	0.80	15.30	3.34 (3.49)	1.77	0.03	11.69
TN (%)	0.34 (0.30)	0.20	0.05	1.13	0.20 (0.17)	0.10	0.04	0.57
C:N	19.41 (4.11)	18.55	12.04	30.43	19.30 (4.45)	18.48	10.36	27.72
TS (%)	0.33 (0.94)	0.07	0.01	4.50	0.07 (0.10)	0.03	0.01	0.45
pH	4.67 (0.74)	4.48	3.43	6.82	4.68 (0.59)	4.69	3.65	6.79
CEC ($cmol_{(c)}\ kg^{-1}$ soil)	10.68 (10.43)	6.78	1.71	37.26	11.76 (13.29)	5.33	1.27	46.33
CECe ($cmol_{(c)}\ kg^{-1}$ soil)	14.12 (17.76)	7.04	3.16	80.35	16.68 (20.16)	6.27	2.40	68.18
Ca^{2+} ($cmol_{(c)}\ kg^{-1}$ soil)	9.19 (17.85)	1.21	0.09	76.23	12.19 (19.56)	1.59	0.00	61.57
Mg^{2+} ($cmol_{(c)}\ kg^{-1}$ soil)	1.01 (1.27)	0.51	0.00	5.39	1.39 (1.92)	0.46	0.00	5.83
Na^{+} ($cmol_{(c)}\ kg^{-1}$ soil)	0.14 (0.20)	0.07	0.05	1.04	0.15 (0.26)	0.08	0.04	1.35
K^{+} ($cmol_{(c)}\ kg^{-1}$ soil)	0.38 (0.43)	0.23	0.09	1.63	0.27 (0.23)	0.18	0.05	1.05
Al^{3+} ($cmol_{(c)}\ kg^{-1}$ soil)	3.39 (2.15)	3.92	0.06	7.16	2.66 (2.51)	1.95	0.01	7.69
%BS	47.65 (35.73)	37.43	4.63	99.88	52.91 (39.67)	55.70	3.59	99.97

Table A.4. Mean, standard deviation (SD) (in brackets), median (Med), minimum (Min) and maximum (Max) of variables analyzed in south transect surface (0- to 5-cm) and sub-surface (5- to 15-cm) mineral samples. Dashes indicate the variable was not measured in that sample (continued).

	Surface				Sub-Surface			
	Mean (SD)	Med	Min	Max	Mean (SD)	Med	Min	Max
% Clay	3.03 (4.03)	0.81	0.00	11.76	3.83 (4.29)	1.73	0.00	13.61

Table A.5. Mean, standard deviation (SD) (in brackets), median (Med), minimum (Min) and maximum (Max) of variables analyzed in south transect surface (0- to 5-cm) and sub-surface (5- to 15-cm) organic samples. Dashes indicate the variable was not measured in that sample.

	Surface				Sub-Surface			
	Mean (SD)	Med	Min	Max	Mean (SD)	Med	Min	Max
WEOC ($mg\ C\ kg^{-1}$ soil)	43.81 (32.55)	38.97	7.38	105.63	59.93 (21.82)	58.56	36.15	85.80
TDN ($mg\ N\ kg^{-1}$ soil)	9.03 (12.06)	2.65	0.43	35.29	6.96 (4.79)	5.74	1.43	13.36
LF-Wt (%)	22.68 (19.92)	18.75	1.03	57.73	-	-	-	-
LF-C (%)	41.75 (8.44)	44.30	21.50	47.50	-	-	-	-
LF-N (%)	1.53 (0.58)	1.43	0.86	2.76	-	-	-	-
LF-C:N	29.51 (9.61)	27.93	16.70	47.22	-	-	-	-
HF-C (%)	22.53 (9.61)	19.20	14.40	33.70	-	-	-	-
HF-N (%)	1.21 (0.65)	0.91	0.70	2.46	-	-	-	-
HF-C:N	20.25 (5.60)	18.32	13.05	30.72	-	-	-	-
TOC (%)	31.36 (10.49)	33.70	19.20	44.93	45.12 (3.95)	46.24	38.99	48.81
TN (%)	1.65 (0.76)	1.51	0.89	3.03	1.80 (0.62)	2.03	0.94	2.36
C:N	20.12 (4.72)	19.18	14.65	30.78	22.31 (9.50)	21.38	11.83	39.73
TS (%)	0.49 (0.29)	0.48	0.06	0.92	1.14 (1.55)	0.58	0.18	4.23
pH	5.27 (0.38)	5.29	4.69	5.83	5.66 (0.42)	5.62	5.20	6.19
CEC ($cmol_{(c)}\ kg^{-1}$ soil)	11.07 (7.46)	9.41	2.79	23.22	10.15 (12.49)	7.72	1.72	34.94
CECe ($cmol_{(c)}\ kg^{-1}$ soil)	22.55 (23.87)	9.98	3.72	62.61	12.82 (15.34)	7.15	2.36	43.36
Ca^{2+} ($cmol_{(c)}\ kg^{-1}$ soil)	14.53 (21.44)	3.53	0.05	55.94	8.28 (15.83)	1.02	0.14	40.12
Mg^{2+} ($cmol_{(c)}\ kg^{-1}$ soil)	2.35 (3.15)	1.02	0.00	8.57	1.12 (1.43)	0.62	0.00	3.49
Na^{+} ($cmol_{(c)}\ kg^{-1}$ soil)	0.14 (0.07)	0.12	0.06	0.25	0.11 (0.06)	0.10	0.05	0.22
K^{+} ($cmol_{(c)}\ kg^{-1}$ soil)	0.39 (0.35)	0.27	0.07	1.08	0.20 (0.19)	0.14	0.08	0.57
Al^{3+} ($cmol_{(c)}\ kg^{-1}$ soil)	2.98 (2.53)	2.92	0.17	7.27	3.11 (2.30)	3.13	0.59	6.35
%BS	62.08 (37.46)	55.57	6.54	99.74	43.45 (41.92)	24.38	6.63	98.03

Table A.6. Spearman's rho correlations between soil organic matter and soil nutrient properties and all properties analyzed in mineral surface (0- to 5-cm) samples. Correlations are based on combined data from the north and south transects and correlations significant at P ≤ 0.05 are in bold; significance values are in brackets.

	WEOC	TDN	LF-Wt	LF-C	LF-N	LF-C:N	HF-C	HF-N	HF-C:N	TOC	TN	C:N	TS
Distance	.027	**-.296**	.072	-.013	-.282	**.320**	-.245	**-.432**	**.592**	-.155	-.233	**.313**	**-.638**
	(.858)	**(.046)**	(.634)	(.931)	(.058)	**(.030)**	(.101)	**(.003)**	**(.000)**	.304	.119	**.034**	**.000**
Ground	**.323**	**-.333**	.059	-.221	**-.322**	**.312**	-.010	-.179	**.411**	.021	-.088	**.368**	-.218
	(.029)	**(.024)**	(.698)	(.139)	**(.029)**	**(.035)**	(.948)	(.234)	**(.005)**	.889	.560	**.012**	.146
Woody	.184	**-.345**	.069	-.286	**-.518**	**.504**	-.263	**-.383**	**.411**	-.186	**-.301**	**.304**	**-.542**
	(.221)	**(.019)**	(.650)	(.054)	**(.000)**	**(.000)**	(.077)	**(.009)**	**(.005)**	.216	**.042**	**.040**	**.000**
WEOC	1.000	.096	**.415**	.157	.034	.065	**.291**	.246	-.107	**.447**	**.391**	.001	.278
		(.527)	**(.004)**	(.298)	(.824)	(.670)	**(.050)**	(.099)	(.480)	**.002**	**.007**	.996	.061
TDN	.096	1.000	.185	.250	**.354**	**-.341**	**.372**	**.384**	**-.345**	**.421**	**.392**	-.204	**.426**
	(.527)		.219	(.093)	**(.016)**	**(.021)**	**(.011)**	**(.008)**	**(.019)**	**.004**	**.007**	.174	**.003**
LF-Wt	**.415**	.185	1.000	**.531**	**.314**	-.146	**.572**	**.480**	-.177	**.748**	**.634**	-.033	**.401**
	.004	(.219)		**(.000)**	**(.033)**	(.334)	**(.000)**	**(.001)**	(.240)	**.000**	**.000**	.829	**.006**
LF-C	.157	.250	**.531**	1.000	**.552**	-.190	**.418**	**.365**	-.197	**.550**	**.458**	-.013	**.325**
	(.298)	(.093)	**.000**		**(.000)**	(.207)	**(.004)**	**(.013)**	(.190)	**.000**	**.001**	.930	**.028**
LF-N	.034	**.354**	**.314**	**.552**	1.000	**-.893**	**.365**	**.416**	**-.389**	**.431**	**.548**	**-.486**	**.582**
	(.824)	**(.016)**	**.033**	**(.000)**		**(.000)**	**(.013)**	**(.004)**	**(.008)**	**.003**	**.000**	**.001**	**.000**
LF-C:N	.065	**-.341**	-.146	-.190	**-.893**	1.000	-.235	**-.326**	**.376**	-.251	**-.412**	**.548**	**-.541**
	(.670)	**(.021)**	.334	(.207)	**(.000)**		(.115)	**(.027)**	**(.010)**	.092	**.004**	**.000**	**.000**
HF-C	**.291**	**.372**	**.572**	**.418**	**.365**	-.235	1.000	**.893**	**-.450**	**.877**	**.831**	-.155	**.681**
	(.050)	**(.011)**	**(.000)**	**(.004)**	**(.013)**	(.115)		**(.000)**	**(.002)**	**.000**	**.000**	.305	**.000**
HF-N	.246	**.384**	**.480**	**.365**	**.416**	**-.326**	**.893**	1.000	**-.779**	**.758**	**.840**	**-.455**	**.771**
	(.099)	**(.008)**	**(.001)**	**(.013)**	**(.004)**	**(.027)**	**(.000)**		**(.000)**	**.000**	**.000**	**.002**	**.000**
HF-C:N	-.107	**-.354**	-.177	-.197	**-.389**	**.376**	**-.450**	**-.779**	1.000	**-.352**	**-.548**	**.720**	**-.653**
	(.480)	**(.019)**	(.240)	(.190)	**(.008)**	**(.010)**	**(.002)**	**(.000)**		**.017**	**.000**	**.000**	**.000**
TOC	**.447**	**.421**	**.748**	**.550**	**.431**	-.251	**.877**	**.758**	**-.352**	1.000	**.909**	-.078	**.681**
	(.002)	**(.004)**	**(.000)**	**(.000)**	**(.003)**	(.092)	**(.000)**	**(.000)**	**(.017)**		**.000**	.605	**.000**
TN	**.391**	**.392**	**.634**	**.458**	**.548**	**-.412**	**.831**	**.840**	**-.548**	**.909**	1.000	**-.415**	**.765**
	(.007)	**(.007)**	**(.000)**	**(.001)**	**(.000)**	**(.004)**	**(.000)**	**(.000)**	**(.000)**	**.000**		**.004**	**.000**
C:N	.001	-.204	-.033	-.013	**-.486**	**.548**	-.155	**-.455**	**.720**	-.078	**-.415**	1.000	**-.457**
	(.996)	(.174)	(.829)	(.930)	**(.001)**	**(.000)**	(.305)	**(.002)**	**(.000)**	.605	**.004**		**.001**

Table A.6. Spearman's rho correlations between soil organic matter and soil nutrient properties and all properties analyzed in mineral surface (0- to 5-cm) samples. Correlations are based on combined data from the north and south transects and correlations significant at P ≤ 0.05 are in bold; significance values are in brackets (continued).

	WEOC	TDN	LF-Wt	LF-C	LF-N	LF-C:N	HF-C	HF-N	HF-C:N	TOC	TN	C:N	TS
TS	.278	**.426**	**.401**	**.325**	**.582**	**-.541**	**.681**	**.771**	**-.653**	**.681**	**.765**	**-.457**	1.000
	(.061)	**(.003)**	**(.006)**	**(.028)**	**(.000)**	**(.000)**	**(.000)**	**(.000)**	**(.000)**	**.000**	**.000**	**.001**	
pH	.156	**-.373**	-.194	**-.569**	**-.406**	.241	**-.370**	**-.419**	**.345**	**-.344**	**-.382**	.244	**-.347**
	(.299)	**(.011)**	(.197)	**(.000)**	**(.005)**	(.106)	**(.011)**	**(.004)**	**(.019)**	**(.019)**	**(.009)**	(.102)	**(.018)**
CEC	-.083	-.131	-.159	-.135	**-.353**	**.334**	-.225	-.274	.247	-.129	-.260	**.438**	-.242
	(.584)	(.386)	(.290)	(.371)	**(.016)**	**(.023)**	(.132)	(.065)	(.099)	(.394)	(.081)	**(.002)**	(.105)
CECe	.123	-.017	.000	-.175	-.001	-.092	.001	.002	-.018	-.013	-.069	.116	.123
	(.415)	(.913)	(.999)	(.245)	(.995)	(.542)	(.993)	(.987)	(.908)	(.929)	(.650)	(.444)	(.416)
Ca^{2+}	-.048	-.105	-.092	-.196	**-.305**	.284	-.065	-.175	.245	-.083	-.198	**.397**	-.222
	(.750)	(.485)	(.544)	(.193)	**(.039)**	(.055)	(.667)	(.245)	(.101)	(.584)	(.188)	**(.006)**	(.138)
Mg^{2+}	-.087	-.115	-.120	-.167	-.252	.224	-.110	-.191	.234	-.123	-.185	**.308**	-.251
	(.565)	(.446)	(.427)	(.267)	(.091)	(.134)	(.468)	(.204)	(.118)	(.415)	(.218)	**(.037)**	(.093)
Na^{+}	.033	.077	.031	-.252	.013	-.104	.008	.042	-.090	.015	-.017	.064	.155
	(.826)	(.612)	(.840)	(.092)	(.930)	(.493)	(.960)	(.782)	(.553)	(.922)	(.910)	(.675)	(.305)
K^{+}	.031	.006	.006	-.097	-.101	.059	-.073	-.108	.139	-.039	-.113	**.296**	-.159
	(.839)	(.967)	(.969)	(.521)	(.503)	(.695)	(.631)	(.476)	(.356)	(.795)	(.453)	**(.046)**	(.290)
Al^{3+}	.179	.149	.140	.076	**.409**	**-.481**	.054	.126	-.194	.071	.137	-.278	**.320**
	(.235)	(.321)	(.352)	(.616)	**(.005)**	**(.001)**	(.719)	(.405)	(.196)	(.637)	(.365)	(.061)	**(.030)**
%BS	-.137	-.177	-.177	-.122	**-.428**	**.478**	-.081	-.189	.281	-.101	-.200	**.392**	**-.350**
	(.363)	(.240)	(.240)	(.419)	**(.003)**	**(.001)**	(.593)	(.207)	(.058)	(.505)	(.182)	**(.007)**	**(.017)**
% Clay	.200	-.064	.076	.116	-.193	.249	.210	.136	-.060	.166	.102	.036	.160
	(.182)	(.674)	(.615)	(.441)	(.200)	(.095)	(.160)	(.367)	(.693)	(.271)	(.501)	(.814)	(.289)

Table A.7. Spearman's rho correlations between exchangeable cations, cation exchange and general soil properties and all analyzed properties measured for mineral surface (0- to 5-cm) samples, based on combined data from the north and south transects. Correlations significant at P ≤ 0.05 are in bold; significance values are in brackets.

	pH	CEC	CECe	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Al^{3+}	%BS	% Clay
Distance	.225	.106	-.237	.097	.155	**-.425**	.061	-.283	**.292**	.103
	(.133)	(.484)	(.112)	(.522)	(.303)	**(.003)**	(.685)	(.057)	**(.049)**	(.495)
Ground	**.584**	.104	.031	**.293**	.233	-.168	.088	**-.316**	**.345**	.144
	(.000)	(.491)	(.837)	**(.048)**	(.120)	(.264)	(.559)	**(.032)**	**(.019)**	(.339)
Woody	**.477**	.191	.216	.108	.059	-.154	.076	-.204	.216	.191
	(.001)	(.203)	(.149)	(.475)	(.695)	(.306)	(.618)	(.175)	(.149)	(.203)
WEOC	.156	-.083	.123	-.048	-.087	.033	.031	.179	-.137	.200
	(.299)	(.584)	(.415)	(.750)	(.565)	(.826)	(.839)	(.235)	(.363)	(.182)
TDN	**-.373**	-.131	-.017	-.105	-.115	.077	.006	.149	-.177	-.064
	(.011)	(.386)	(.913)	(.485)	(.446)	(.612)	(.967)	(.321)	(.240)	(.674)
LF-Wt	-.194	-.159	.000	-.092	-.120	.031	.006	.140	-.177	.076
	(.197)	(.290)	(.999)	(.544)	(.427)	(.840)	(.969)	(.352)	(.240)	(.615)
LF-C	**-.569**	-.135	-.175	-.196	-.167	-.252	-.097	.076	-.122	.116
	(.000)	(.371)	(.245)	(.193)	(.267)	(.092)	(.521)	(.616)	(.419)	(.441)
LF-N	**-.406**	**-.353**	-.001	**-.305**	-.252	.013	-.101	**.409**	**-.428**	-.193
	(.005)	**(.016)**	(.995)	**(.039)**	(.091)	(.930)	(.503)	**(.005)**	**(.003)**	(.200)
LF-C:N	.241	**.334**	-.092	.284	.224	-.104	.059	**-.481**	**-.478**	.249
	(.106)	**(.023)**	(.542)	(.055)	(.134)	(.493)	(.695)	**(.001)**	**(.001)**	(.095)
HF-C	**-.370**	-.225	.001	-.065	-.110	.008	-.073	.054	-.081	.210
	(.011)	(.132)	(.993)	(.667)	(.468)	(.960)	(.631)	(.719)	(.593)	(.160)
HF-N	**-.419**	-.274	.002	-.175	-.191	.042	-.108	.126	-.189	.136
	(.004)	(.065)	(.987)	(.245)	(.204)	(.782)	(.476)	(.405)	(.207)	(.367)
HF-C:N	**.345**	.247	-.018	.245	.234	-.090	.139	-.194	.281	-.060
	(.019)	(.099)	(.908)	(.101)	(.118)	(.553)	(.356)	(.196)	(.058)	(.693)
TOC	**-.344**	-.129	-.013	-.083	-.123	.015	-.039	.071	-.101	.166
	(.019)	(.394)	(.929)	(.584)	(.415)	(.922)	(.795)	(.637)	(.505)	(.271)
TN	**-.382**	-.260	-.069	-.198	-.185	-.017	-.113	.137	-.200	-.260
	(.009)	(.081)	(.650)	(.188)	(.218)	(.910)	(.453)	(.365)	(.182)	(.081)
C:N	.244	**.438**	.116	**.397**	**.308**	.064	**.296**	-.278	**.392**	**.438**
	(.102)	**(.002)**	(.444)	**(.006)**	**(.037)**	(.675)	**(.046)**	(.061)	**(.007)**	**(.002)**

Table A.7. Spearman's rho correlations between exchangeable cations, cation exchange and general soil properties and all analyzed properties measured for mineral surface (0- to 5-cm) samples, based on combined data from the north and south transects. Correlations significant at P ≤ 0.05 are in bold; significance values are in brackets (continued).

	pH	CEC	CECe	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Al^{3+}	%BS	% Clay
TS	**-.347**	-.242	.123	-.222	-.251	.155	-.159	**.320**	**-.350**	-.242
	(.018)	(.105)	(.416)	(.138)	(.093)	(.305)	(.290)	**(.030)**	**(.017)**	(.105)
pH	1.000	.216	.269	.257	.185	.183	.184	-.061	.148	-.044
		(.150)	(.071)	(.085)	(.220)	(.223)	(.221)	(.688)	(.326)	(.773)
CEC	.216	1.000	**.528**	**.713**	**.661**	**.350**	**.652**	**-.538**	**.696**	.244
	(.150)		**(.000)**	**(.000)**	**(.000)**	**(.017)**	**(.000)**	**(.000)**	**(.000)**	(.102)
CECe	.269	**.528**	1.000	**.666**	**.644**	**.751**	**.750**	.089	.241	.071
	(.071)	**(.000)**		**(.000)**	**(.000)**	**(.000)**	**(.000)**	(.556)	(.106)	(.641)
Ca^{2+}	.257	**.713**	**.666**	1.000	**.925**	**.484**	**.770**	**-.561**	**.816**	.165
	(.085)	**(.000)**	**(.000)**		**(.000)**	**(.001)**	**(.000)**	**(.000)**	**(.000)**	(.273)
Mg^{2+}	.185	**.661**	**.644**	**.925**	1.000	**.467**	**.806**	**-.544**	**.776**	.124
	(.220)	**(.000)**	**(.000)**	**(.000)**		**(.001)**	**(.000)**	**(.000)**	**(.000)**	(.412)
Na^{+}	.183	**.350**	**.751**	**.484**	**.467**	1.000	**.542**	.158	.072	-.226
	(.223)	**(.017)**	**(.000)**	**(.001)**	**(.001)**		**(.000)**	(.295)	(.632)	(.131)
K^{+}	.184	**.652**	**.750**	**.770**	**.806**	**.542**	1.000	-.211	**.511**	-.033
	(.221)	**(.000)**	**(.000)**	**(.000)**	**(.000)**	**(.000)**		(.160)	**(.000)**	(.827)
Al^{3+}	-.061	**-.538**	.089	**-.561**	**-.544**	.158	-.211	1.000	**.902**	**-.293**
	(.688)	**(.000)**	(.556)	**(.000)**	**(.000)**	(.295)	(.160)		**(.000)**	**(.048)**
%BS	.148	**.696**	.241	**.816**	**.776**	.072	**.511**	**.902**	1.000	**.315**
	(.326)	**(.000)**	(.106)	**(.000)**	**(.000)**	(.632)	**(.000)**	**(.000)**		**(.033)**
% Clay	-.044	.244	.071	.165	.124	-.226	-.033	**-.293**	**.315**	1.000
	(.773)	(.102)	(.641)	(.273)	(.412)	(.131)	(.827)	**(.048)**	**(.033)**	

Table A.8. Spearman's rho correlations between soil organic matter and soil nutrient properties with all analyzed properties measured for mineral sub-surface (5- to 15-cm) samples based on combined data from the north and south transects. Correlations significant at P ≤ 0.05 are in bold; significance values are in brackets.

	WEOC	TDN	TOC	TN	C:N	TS
Distance	**-.305**	**-.461**	**-.465**	**–.327**	-.095	**-.592**
	(.031)	**(.001)**	**(.001)**	**(.020)**	(.513)	**(.000)**
Ground	-.020	**-.289**	-.091	-.109	.177	-.240
	(.889)	**(.042)**	(.530)	(.452)	(.218)	(.093)
Woody	.052	**-.423**	-.257	-.210	.041	**-.463**
	(.721)	**(.002)**	(.072)	(.144)	(.777)	**(.001)**
WEOC	1.000	**.377**	**.622**	**.520**	.088	**.470**
		(.007)	**(.000)**	**(.000)**	(.545)	**(.001)**
TDN	**.377**	1.000	**.575**	**.480**	-.030	**.453**
	(.007)		**(.000)**	**(.000)**	(.836)	**(.001)**
TOC	**.622**	**.575**	1.000	**.887**	.086	**.777**
	(.000)	**(.000)**		**(.000)**	(.554)	**(.000)**
TN	**.520**	**.480**	**.887**	1.000	**–.299**	**.767**
	(.000)	**(.000)**	**(.000)**		**(.035)**	**(.000)**
C:N	.088	-.030	.086	**-.299**	1.000	-.138
	(.545)	(.836)	(.554)	**(.035)**		(.339)
TS	**.470**	**.453**	**.777**	**.767**	-.138	1.000
	(.001)	**(.001)**	**(.000)**	**(.000)**	(.339)	
pH	-.059	**-.431**	**-.319**	-.259	-.001	**-.338**
	(.684)	**(.002)**	**(.024)**	(.069)	(.996)	**(.016)**
CEC	.005	-.243	-.015	.002	.125	-.122
	(.974)	(.089)	(.916)	(.991)	(.388)	(.399)
CECe	.109	-.091	.153	.185	-.017	.167
	(.451)	(.531)	(.289)	(.199)	(.909)	(.246)
Ca^{2+}	-.115	-.225	.035	.031	.064	-.104
	(.428)	(.116)	(.808)	(.828)	(.657)	(.470)
Mg^{2+}	-.169	-.235	-.019	.028	.023	-.127
	(.240)	(.100)	(.898)	(.846)	(.875)	(.380)
Na^{+}	.143	.031	.151	.169	-.070	.188
	(.320)	(.831)	(.297)	(.241)	(.628)	(.192)
K^{+}	.033	-.207	.070	.142	-.023	.054
	(.823)	(.150)	(.630)	(.327)	(.873)	(.712)
Al^{3+}	.171	.216	-.040	-.075	-.023	.151
	(.235)	(.132)	(.785)	(.603)	(.876)	(.296)
%BS	-.214	-.259	-.013	.024	.010	-.189
	(.135)	(.069)	(.930)	(.869)	(.943)	(.189)
% Clay	.032	-.248	.012	.038	-.031	-.004
	(.823)	(.083)	(.936)	(.792)	(.831)	(.978)

Table A.9. Spearman's rho correlations between exchangeable cations, cation exchange and general soil properties with all analyzed properties measured for mineral sub-surface (5- to 15-cm) samples based on combined data from the north and south transects. Correlations significant at P ≤ 0.05 are in bold; significance values are in brackets.

	pH	CEC	CECe	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Al^{3+}	%BS	% Clay
Distance	**.417**	.050	**-.398**	.028	.162	**-.407**	-.072	**-.412**	**.353**	.245
	(.003)	(.729)	**(.004)**	(.845)	(.263)	**(.003)**	(.617)	**(.003)**	**(.012)**	(.086)
Ground	**.550**	.143	-.067	**.282**	.266	-.164	.006	**-.362**	**.343**	.184
	(.000)	(.321)	(.644)	**(.047)**	(.062)	(.254)	(.969)	**(.010)**	**(.015)**	(.201)
Woody	**.615**	.224	-.172	.088	.173	-.171	-.036	**-.342**	.277	.204
	(.000)	(.118)	(.232)	(.544)	(.230)	(.235)	(.806)	**(.015)**	(.051)	(.156)
WEOC	-.059	.005	.109	-.115	-.169	.143	.033	.171	-.214	.032
	(.684)	(.974)	(.451)	(.428)	(.240)	(.320)	(.823)	(.235)	(.135)	(.823)
TDN	**-.431**	-.243	-.091	-.225	-.235	.031	-.207	.216	-.259	-.248
	(.002)	(.089)	(.531)	(.116)	(.100)	(.831)	(.150)	(.132)	(.069)	(.083)
TOC	**-.319**	-.015	.153	.035	-.019	.151	.070	-.040	-.013	.012
	(.024)	(.916)	(.289)	(.808)	(.898)	(.297)	(.630)	(.785)	(.930)	(.936)
TN	-.259	.002	.185	.031	.028	.169	.142	-.075	.024	.038
	(.069)	(.991)	(.199)	(.828)	(.846)	(.241)	(.327)	(.603)	(.869)	(.792)
C:N	-.001	.125	-.017	.064	.023	-.070	-.023	-.023	.010	-.031
	(.996)	(.388)	(.909)	(.657)	(.875)	(.628)	(.873)	(.876)	(.943)	(.831)
TS	**-.338**	-.122	.167	-.104	-.127	.188	.054	.151	-.189	-.004
	(.016)	(.399)	(.246)	(.470)	(.380)	(.192)	(.712)	(.296)	(.189)	(.978)
pH	1.000	**.371**	068	.277	**.286**	.057	.145	**-.323**	**.304**	.148
		(.008)	(.638)	(.051)	**(.044)**	(.693)	(.314)	**(.022)**	**(.032)**	(.306)
CEC	**.371**	1.000	**.504**	**.669**	**.650**	**.374**	**.661**	**.504**	**.607**	.076
	(.008)		**(.000)**	**(.000)**	**(.000)**	**(.007)**	**(.000)**	**(.000)**	**(.000)**	(.601)
CECe	.068	**.504**	1.000	**.562**	**.504**	**.747**	**.623**	.091	.105	-.105
	(.638)	**(.000)**		**(.000)**	**(.000)**	**(.000)**	**(.000)**	(.531)	(.468)	(.467)
Ca^{2+}	.277	**.669**	**.650**	1.000	**.925**	**.522**	**.679**	**-.577**	**.745**	-.066
	(.051)	**(.000)**	**(.000)**		**(.000)**	**(.000)**	**(.000)**	**(.000)**	**(.000)**	(.649)
Mg^{2+}	**.286**	**.650**	**.504**	**.925**	1.000	**.482**	**.681**	**-.633**	**.763**	-.045
	(.044)	**(.000)**	**(.000)**	**(.000)**		**(.000)**	**(.000)**	**(.000)**	**(.000)**	(.758)
Na^{+}	.057	**.374**	**.747**	**.522**	**.482**	1.000	**.526**	.032	.099	-.268
	(.693)	**(.007)**	**(.000)**	**(.000)**	**(.000)**		**(.000)**	(.825)	(.495)	(.060)

Table A.9. Spearman's rho correlations between exchangeable cations, cation exchange and general soil properties with all analyzed properties measured for mineral sub-surface (5- to 15-cm) samples based on combined data from the north and south transects. Correlations significant at P ≤ 0.05 are in bold; significance values are in brackets (continued).

	pH	CEC	CECe	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Al^{3+}	%BS	% Clay
K^{+}	.145	**.661**	**.623**	**.679**	**.681**	**.526**	1.000	-.268	**.442**	-.176
	(.314)	**(.000)**	**(.000)**	**(.000)**	**(.000)**	**(.000)**		(.060)	**(.001)**	(.222)
Al^{3+}	**-.323**	**.504**	.091	**-.577**	**-.633**	.032	-.268	1.000	**-.945**	-.065
	(.022)	**(.000)**	(.531)	**(.000)**	**(.000)**	(.825)	(.060)		**(.000)**	(.655)
%BS	**.304**	**.607**	.105	**.745**	**.763**	.099	**.442**	**-.945**	1.000	.041
	(.032)	**(.000)**	(.468)	**(.000)**	**(.000)**	(.495)	**(.001)**	**(.000)**		(.775)
% Clay	.148	.076	-.105	-.066	-.045	-.268	-.176	-.065	.041	1.000
	(.306)	(.601)	(.467)	(.649)	(.758)	(.060)	(.222)	(.655)	(.775)	

Table A.10. Spearman's rho correlations between soil organic matter and soil nutrient properties with all analyzed properties measured for organic surface (0- to 5-cm) samples based on combined data from the north and south transects. Correlations significant at $P \leq 0.05$ are in bold; significance values are in brackets.

	WEOC	TDN	LF-Wt	LF-C	LF-N	LF-C:N	HF-C	HF-N	HF-C:N	TOC	TN	C:N	TS
Distance	-.063	.178	.329	.116	-.150	-.209	**.606**	.461	-.181	.320	.169	-.133	-.003
	(.816)	(.508)	(.214)	(.668)	(.580)	(.437)	**(.013)**	(.072)	(.502)	(.227)	(.532)	(.624)	(.991)
Ground	.446	**.554**	.468	.156	-.196	.075	.403	.154	.240	.352	.081	.323	.366
	(.083)	**(.026)**	(.068)	(.564)	(.467)	(.783)	(.122)	(.568)	(.370)	(.181)	(.765)	(.222)	(.163)
Woody	-.058	-.381	-.216	.480	-.266	.360	-.204	-.342	.298	-.164	-.441	.253	-.052
	(.832)	(.146)	(.421)	(.060)	(.319)	(.171)	(.448)	(.195)	(.263)	(.543)	(.087)	(.344)	(.849)
WEOC	1.000	**.636**	.415	.285	.493	**-.518**	.012	.232	-.235	.294	**.597**	-.326	**.792**
		(.008)	(.110)	(.284)	(.052)	**(.040)**	(.966)	.387	(.380)	(.269)	**(.015)**	(.217)	**(.000)**
TDN	**.636**	1.000	**.509**	.007	.479	**-.562**	.313	**.550**	-.416	.387	**.647**	-.306	.465
	(.008)		**(.044)**	(.978)	(.061)	**(.023)**	.237	**.027**	.109	(.139)	**(.007)**	(.249)	(.069)
LF-Wt	.415	**.509**	1.000	.188	.206	-.435	**.656**	**.668**	-.235	**.774**	**.624**	-.091	.409
	(.110)	**(.044)**		(.485)	(.444)	(.092)	**(.006)**	**(.005)**	(.380)	**(.000)**	**(.010)**	(.737)	(.116)
LF-C	.285	.007	.188	1.000	.449	.047	-.121	-.168	.115	.241	-.060	.185	.253
	(.284)	(.978)	(.485)		(.081)	(.863)	(.656)	(.535)	(.672)	(.368)	(.824)	(.492)	(.344)
LF-N	.493	.479	.206	.449	1.000	**-.597**	-.203	.224	**-.512**	.155	.493	-.449	.292
	(.052)	(.061)	(.444)	(.081)		**(.015)**	(.451)	(.405)	**(.043)**	(.568)	(.052)	(.081)	(.273)
LF-C:N	**-.518**	**-.562**	-.435	.047	**-.597**	1.000	-.165	**-.676**	**.885**	-.132	**-.829**	**.850**	**-.524**
	(.040)	**(.023)**	(.092)	(.863)	**(.015)**		(.542)	**(.004)**	**(.000)**	(.625)	**(.000)**	**(.000)**	**(.037)**
HF-C	.012	.313	**.656**	-.121	-.203	-.165	1.000	**.756**	-.062	**.738**	.475	.079	.106
	(.966)	(.237)	**(.006)**	(.656)	(.451)	(.542)		**(.001)**	(.820)	**(.001)**	(.063)	(.770)	(.696)
HF-N	.232	**.550**	**.668**	-.168	.224	**-.676**	**.765**	1.000	**.-647**	**.521**	**.824**	-.497	.218
	(.387)	**(.027)**	**(.005)**	(.535)	(.405)	**(.004)**	**(.001)**		**(.007)**	**(.039)**	**(.0000**	(.050)	(.418)
HF-C:N	-.235	-.416	-.235	.115	**-.512**	**.885**	-.062	**-.647**	1.000	.126	**-.643**	**.935**	-.238
	(.380)	(.109)	(.380)	(.672)	**(.043)**	**(.000)**	(.820)	**(.007)**		(.641)	**(.007)**	**(.000)**	(.374)
TOC	.294	.387	**.774**	.241	.155	-.132	**.738**	**.521**	.126	1.000	**.517**	.241	.327
	(.269)	(.139)	**(.000)**	(.368)	(.568)	(.625)	**(.001)**	**(.039)**	(.641)		**(.040)**	(.368)	(.217)
TN	**.597**	**.647**	**.624**	-.060	.493	**-.829**	.475	**.824**	**-.643**	**.517**	1.000	**-.596**	**.588**
	(.015)	**(.007)**	**(.010)**	(.824)	(.052)	**(.000)**	(.063)	**(.000)**	**(.007)**	**(.040)**		**(.015)**	**(.017)**
C:N	-.326	-.306	-.091	.185	-.449	**.850**	.079	-.497	**.935**	.241	**-.596**	1.000	-.297
	(.217)	(.249)	(.737)	(.492)	(.081)	**(.000)**	(.770)	(.050)	**(.000)**	(.368)	**(.015)**		(.263)

Table A.10. Spearman's rho correlations between soil organic matter and soil nutrient properties with all analyzed properties measured for organic surface (0- to 5-cm) samples based on combined data from the north and south transects. Correlations significant at $P \leq 0.05$ are in bold; significance values are in brackets (continued).

	WEOC	TDN	LF-Wt	LF-C	LF-N	LF-C:N	HF-C	HF-N	HF-C:N	TOC	TN	C:N	TS
TS	**.792**	.465	.409	.253	.292	**-.524**	.106	.218	-.238	.327	**.588**	-.297	1.000
	(.000)	(.069)	(.116)	(.344)	(.273)	**(.037)**	(.696)	(.418)	(.374)	(.217)	**(.017)**	(.263)	
pH	.130	.233	**.657**	.121	-.175	-.052	**.778**	.454	.221	**.809**	.411	.336	.371
	(.632)	(.385)	**(.006)**	(.656)	(.516)	(.850)	**(.000)**	(.078)	(.411)	**(.000)**	(.114)	(.204)	(.158)
CEC	**-.532**	-.172	-.238	-.226	-.122	-.150	.088	.247	-.329	-.185	.057	-.276	-.440
	(.034)	(.524)	(.374)	(.399)	(.652)	(.579)	(.745)	(.356)	(.213)	(.492)	(.833)	(.300)	(.088)
CECe	-.247	-.109	.374	-.041	.168	-.268	-.226	.079	-.388	-.353	.135	-.403	-.200
	(.356)	(.688)	(.154)	(.880)	(.535)	(.361)	(.399)	(.770)	(.137)	(.180)	(.617)	(.122)	(.457)
Ca^{2+}	-.429	-.193	-.335	.112	.131	-.100	-.091	.062	-.256	-.224	-.003	-.194	-.325
	(.097)	(.474)	(.204)	(680)	(.629)	(.713)	(.737)	(.820)	(.339)	(.405)	(.991)	(.471)	(.219)
Mg^{2+}	-.339	-.106	-.268	-.136	.013	-.201	.032	.212	-.316	-.168	.134	-.307	-.332
	(.199)	(.695)	(.315)	(.616)	(.961)	(.456)	(.905)	(.430)	(.234)	(.534)	(.620)	(.248)	(.209)
Na^{+}	-.222	-.275	**-.663**	-.377	-.128	-.001	**-.611**	-.364	-.134	**-.670**	-.186	-.253	-.165
	(.408)	(.303)	**(.005)**	(.150)	(.636)	(.996)	**.012**	.166	(.621)	**(.005)**	(.489)	(.344)	(.541)
K^{+}	-.415	-.059	-.171	.015	.021	-.074	.056	.147	-.221	-.032	-.016	-.153	-.415
	(.110)	(.829)	(.528)	(.957)	(.940)	(.787)	(.837)	(.587)	(.412)	(.905)	(.953)	(.572)	(.110)
Al^{3+}	**.690**	.217	.202	.028	.088	-.241	-.268	-.159	.047	-.016	.203	-.112	**.563**
	(.003)	(.419)	(.454)	(.918)	(.747)	(.368)	(.316)	(.557)	(.863)	(.953)	(.450)	(.680)	**(.023)**
%BS	**-.596**	-.114	-.110	.075	.055	.003	.303	.291	-.191	.104	.022	-.015	-.404
	(.015)	(.674)	(.684)	(.782)	(.839)	(.991)	(.254)	(.274)	(.487)	(.700)	(.935)	(.957)	(.121)

Table A.11. Spearman's rho correlations between exchangeable cations, cation exchange and general soil properties with all analyzed properties measured for organic surface (0- to 5-cm) samples based on combined data from the north and south transects. Correlations significant at P ≤ 0.05 are in bold; significance values are in brackets.

	pH	CEC	CECe	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Al^{3+}	%BS
Distance	.415	.416	.196	.342	.375	-.382	.445	-.337	.456
	(1.09)	(.076)	(.467)	(.195)	(.152)	(.214)	(.084)	(.202)	(.076)
Ground	.411	-.476	-.497	-.484	-.405	-.472	-.317	.286	-.356
	(.114)	(.063)	(.050)	(.058)	(.119)	(.065)	(.232)	(.283)	(.176)
Woody	-.003	-.022	-.031	.044	-.131	-.111	-.053	.061	-.025
	(.991)	(.935)	(.909)	(.870)	(.630)	(.682)	(.845)	(.823)	(.926)
WEOC	.130	**.532**	.247	-.429	-.339	-.222	-.415	**.690**	**.596**
	(.632)	**(.034)**	(.356)	(.097)	(.199)	(.408)	(.110)	**(.003)**	**(.015)**
TDN	. 233	.172	-.109	-.193	-.106	-.275	-.059	.217	-.114
	(.385)	(.524)	(.688)	(.474)	(.695)	(.303)	(.829)	(.419)	(.674)
TOC	**.809**	-.185	-.353	-.244	-.168	**-.670**	-.032	-.016	.104
	(.000)	(.492)	(.180)	(.405)	(.534)	**(.005)**	(.905)	(953)	(.700)
TN	.411	.057	.135	-.003	.134	-.186	-.016	.203	.022
	(.114)	(.833)	(.617)	(.991)	(.620)	(.489)	(.953)	(.450)	(.935)
C:N	.336	-.276	-.403	-.194	-.307	-.253	-.153	-.112	-.015
	(.204)	(.300)	(.122)	(.471)	(.471)	(.344)	(.572)	(.680)	(.957)
TS	.371	-.440	-.200	-.325	-.332	-.165	-.415	**.563**	-.404
	(.158)	(.088)	(.457)	(.219)	(.219)	(.541)	(.110)	**(.023)**	(.121)
pH	1.000	-.065	-.240	-.113	-.136	**-.571**	-.124	.021	.158
		(.812)	(.370)	(.676)	(.616)	**(.021)**	(.648)	(.940)	(.560)
CEC	-.065	1.000	**.815**	**.853**	**.923**	**.499**	**.879**	**-.515**	**.724**
	(.812)		**(.000)**	**(.000)**	**(.000)**	**(.049)**	**(.000)**	**(.041)**	**(.002)**
CECe	-.240	**.815**	1.000	**.897**	**.894**	**.601**	**.685**	-.352	**.596**
	(.437)	**(.000)**		**(.000)**	**(.000)**	**(.014)**	**(.003)**	(.182)	**(.015)**
Ca^{2+}	-.113	**.853**	**.897**	1.000	**.876**	.476	**.794**	**-.612**	**.815**
	(.676)	**(.000)**	**(.000)**		**(.000)**	(.063)	**(.000)**	**(.012)**	**(.000)**
Mg^{2+}	-.136	**.923**	**.894**	**.876**	1.000	**.548**	**.888**	-.455	**.655**
	(.616)	**(.000)**	**(.000)**	**(.000)**		**(.028)**	**(.000)**	(.077)	**(.006)**
Na^{+}	**-.571**	**.499**	**.601**	.476	**.548**	1.000	.420	.003	.049
	(.021)	**(.049)**	**(.014)**	(.063)	**(.028)**		(.106)	(.991)	(.858)

Table A.11. Spearman's rho correlations between exchangeable cations, cation exchange and general soil properties with all analyzed properties measured for organic surface (0- to 5-cm) samples based on combined data from the north and south transects. Correlations significant at P ≤ 0.05 are in bold; significance values are in brackets (continued).

	pH	CEC	CECe	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Al^{3+}	%BS
K^{+}	-.124	**.879**	**.685**	**.794**	**.888**	.420	1.000	**-.524**	**.677**
	(.648)	**(.000)**	**(.003)**	**(.000)**	**(.000)**	(.106)		**(.037)**	**(.004)**
Al^{3+}	.021	**.515**	-.352	**-.612**	-.455	.003	**-.524**	1.000	**-.894**
	(.940)	**(.014)**	(.182)	**(.012)**	(.077)	(.991)	**(.037)**		**(.000)**
%BS	.158	**.724**	**.596**	**.815**	**.655**	.049	**.667**	**-.894**	1.000
	(.560)	**(.002)**	**(.015)**	**(.000)**	**(.006)**	(.858)	**(.004)**	**(.000)**	

Table A.12. Spearman's rho correlations between soil organic matter and soil nutrient properties with all analyzed properties measured for organic sub-surface (5- to 15-cm) samples based on combined data from the north and south transects. Correlations significant at P ≤ 0.05 are in bold; significance values are in brackets.

	WEOC	TDN	TOC	TN	C:N	TS
Distance	.291	.182	.046	.445	-.214	-.067
	(.359)	(.571)	(.888)	(.147)	(.505)	(.837)
Ground	-.045	.124	-.196	.023	**-.592**	.253
	(.889)	(.700)	(.541)	(.944)	**(.043)**	(.421)
Woody	.349	-.171	.199	-.082	-.174	.149
	(.266)	(.595)	(.535)	(.800)	(.588)	(.643)
WEOC	1.000	.448	.524	.077	.378	-.182
		(.145)	(.080)	(.812)	(.226)	(.572)
TDN	.448	1.000	.210	.406	-.147	.007
	(.145)		(.513)	(.191)	(.649)	(.983)
TOC	.524	.210	1.000	.364	-.042	.455
	(.080)	(.513)		(.245)	(.897)	(.138)
TN	.077	.406	.364	1.000	-.420	.371
	(.812)	(.191)	(.245)		(.175)	(.236)
C:N	.378	-.147	-.042	-.420	1.000	**-.769**
	(.226)	(.649)	(.897)	(.175)		**(.003)**
TS	-.182	.007	.455	.371	**-.769**	1.000
	(.572)	(.983)	(.138)	(.236)	**(.003)**	
pH	-.161	.098	**-.608**	.154	-.028	-.434
	(.618)	(.762)	**(.036)**	(.633)	(.931)	(.159)
CEC	-.140	-.196	.140	.573	-.077	.091
	(.665)	(.542)	(.665)	(.051)	(.812)	(.779)
CECe	.021	.196	.133	.483	.021	.056
	(.948)	(.542)	(.681)	(.112)	(.948)	(.863)
Ca^{2+}	.021	.014	.308	.685	-.056	.077
	(.948)	(.966)	(.331)	(.014)	(.863)	(.812)
Mg^{2+}	.152	.058	.123	.493	.036	-.073
	(.637)	(.858)	(.703)	(.103)	(.911)	(.823)
Na^{+}	.049	.154	-.084	.203	-.119	.084
	(.880)	(.633)	(.795)	(.527)	(.713)	(.795)
K^{+}	.084	.308	.000	.343	.084	-.259
	(.795)	(.331)	(1.000)	(.276)	(.795)	(.417)
Al^{3+}	-.021	.287	-.224	-.294	-.126	.196
	(.948)	(.366)	(.484)	(.354)	(.697)	(.542)
%BS	-.035	-.112	.189	**.671**	.035	-.084
	(.914)	(.729)	(.557)	**(.017)**	(.914)	(.795)

Table A.13. Spearman's rho correlations between exchangeable cations, cation exchange and general soil properties with all analyzed properties measured for organic sub0surface (5- to 15-cm) samples based on combined data from the north and south transects. Correlations significant at P ≤ 0.05 are in bold; significance values are in brackets.

	pH	CEC	CECe	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Al^{3+}	%BS
Distance	.424	.039	-.109	.165	.320	-.102	.256	-.343	.375
	(.170)	(.905)	(.737)	(.609)	(.311)	(.753)	(.422)	(.275)	(.230)
Ground	.424	-.483	-.569	-.467	-.395	-.305	-.441	.313	-.411
	(.170)	(.112)	(.053)	(.125)	(.204)	(.334)	(.151)	(.322)	(.184)
Woody	.260	-.171	-.463	-.125	-.159	-.174	-.384	-.068	-.128
	(.414)	(.595)	(.130)	(.700)	(.622)	(.588)	(.214)	(.835)	(.691)
WEOC	-.161	-.140	.021	.021	.152	.049	.084	-.021	-.035
	(.618)	(.665)	(.948)	(.948)	(.637)	(.880)	(.795)	(.948)	(.914)
TDN	.098	-.196	.196	.014	.058	.154	.308	.287	-.112
	(.762)	(.542)	(.542)	(.966)	(.858)	(.633)	(.331)	(.366)	(.729)
TOC	**-608**	.140	.133	.308	.123	-.084	.000	-.224	.189
	(.036)	(.665)	(.681)	(.331)	(.703)	(.795)	(1.000)	(.484)	(.557)
TN	.154	.573	.483	.685	.493	.203	.343	-.294	**.671**
	(.633)	(.051)	(.112)	(.014)	(.103)	(.527)	(.276)	(.354)	**(.017)**
C:N	-.028	-.077	.021	-.056	.036	-.119	.084	-.126	.035
	(.931)	(.812)	(.948)	(.863)	(.911)	(.713)	(.795)	(.697)	(.914)
TS	-.434	.091	.056	.077	-.073	.084	-.259	.196	-.084
	(.159)	(.779)	(.863)	(.812)	(.823)	(.795)	(.417)	(.542)	(.795)
pH	1.000	-.063	-.280	-.084	-.087	-.217	.070	.035	.126
		.846	.379	.795	.788	.499	.829	.914	.697
CEC	-.063	1.000	**.797**	**.937**	**.805**	**.601**	**.580**	-.510	**.839**
	(.846)		**(.002)**	**(.000)**	**(.002)**	**(.039)**	**(.048)**	(.090)	**(.001)**
CECe	-.280	**.797**	1.000	**.811**	**.841**	**.846**	**.699**	-.189	.573
	(.379)	**(.002)**		**(.001)**	**(.001)**	**(.001)**	**(.011)**	(.557)	(.051)
Ca^{2+}	-.084	**.937**	**.811**	1.000	**.877**	**.587**	**.664**	**-.608**	**.902**
	(.795)	**(.000)**	**(.001)**		**(.000)**	**(.045)**	**(.018)**	**(.036)**	**(.000)**
Mg^{2+}	-.087	**.805**	**.841**	**.877**	1.000	**.776**	**.798**	-.515	**.776**
	(.788)	**(.002)**	**(.001)**	**(.000)**		**(.003)**	**(.002)**	(.087)	**(.003)**
Na^{+}	-.217	**.601**	**.846**	**.587**	**.776**	1.000	**.622**	-.014	.294
	(.499)	**(.039)**	**(.001)**	**(.045)**	**(.003)**		**(.031)**	(.966)	(.353)

Table A.13. Spearman's rho correlations between exchangeable cations, cation exchange and general soil properties with all analyzed properties measured for organic sub0surface (5- to 15-cm) samples based on combined data from the north and south transects. Correlations significant at P ≤ 0.05 are in bold; significance values are in brackets (continued).

	pH	CEC	CECe	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Al^{3+}	%BS
K^{+}	.070	**.580**	**.699**	**.664**	**.798**	**.622**	1.000	-.336	**.601**
	(.829)	**(.048)**	**(.011)**	**(.018)**	**(.002)**	**(.031)**		(.286)	**(.039)**
Al^{3+}	.035	-.510	-.189	**-.608**	-.515	-.014	-.336	1.000	**-.797**
	(.914)	(.090	(.557)	**(.036)**	(.087)	(.966)	(.286)		**(.002)**
%BS	.126	**.839**	.573	**.902**	**.776**	.294	**.601**	**-.797**	1.000
	(.697)	**(.001)**	(.051)	**(.000)**	**(.003)**	(.354)	**(.039)**	**(.002)**	